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POLLUTANT ANALYSIS COST SURVEY

National Bureau of Standards

December 1974

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POLLUTANT ANALYSIS COST SURVEY

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This report supersedes NBSIR 73-209, "Survey of Various Approaches to the Chemical Analysis of Environmentally Important Materials", of which it is a revision and extension.

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POLLUTANT ANALYSIS COST SURVEY

Final Report
June 1972 - June 1974

by

Bernard Greifer and John K. Taylor

ABSTRACT

The report summarizes various approaches to the chemical analysis of heavy industry process materials and effluents for trace element constituents that might contribute to environmental pollution. It assesses the capabilities and costs of nuclear methods, spark source mass spectrometry, x-ray fluorescence and electron and ion microprobe spectrometry, atomic absorption spectrometry, absorption spectrophotometry, atomic emission spectroscopy, voltammetry (polarography) and potentiometry (ion-selective electrodes) for determining traces (less than 100 ppm) of Hg, Be, Cd, As, V, Mn, Ni, Sb. Cr, Zn, Cu, Pb, Se, B, F, Li, Ag, Sn, Fe, Sr, Na, K, Ca, Si, Mg, U, and Th in such matrices as fly ash, coal, oil, ores, minerals, metals, alloys, organometallics, incinerator particulates, slurry streams, and feeds to and from sedimentation processes. The report includes a selected bibliography of the current literature, and a review of the Standard Reference Materials available for environmental analysis.

This report supersedes NBSIR 73-209, "Survey of Various Approaches to the Chemical Analysis of Environmentally Important Materials", of which it is a revision and extension.

CHAPTER 1

INTRODUCTION

Bernard Greifer

1. REPORT FORMAT

This report is an evaluation of various approaches to the chemical analysis of heavy industry process materials and waste products for constituents that may find their way into the environment and be considered pollutants. The applicability and costs of suitable methods of measuring the trace metal content (less than 100 ppm) of industrial process feeds, product streams, and effluents are presented for comparison so that the optimum analytical support programs for particular situations can be selected from among the available alternatives.

Heavy industrial processes have come under scrutiny as contributors to environmental contamination. While sulfur dioxide and particulate emissions have been investigated extensively, the trace elements in these and other effluents have been relatively unexplored. These trace elements may be a source of valuable by-products that could be recovered, or they may constitute a toxic hazard that should be removed; but they ought not to remain an unknown quantity. Modern instrumental methods of analysis have the capability to determine the trace elements in industrial effluents at a reasonable cost. This report summarizes current procedures suitable for the analysis of these and similar materials.

The information provided is based on a bibliographic survey and evaluation of the current literature by members of the staff of the Analytical Chemistry Division, Institute for Materials Research, of the National Bureau of Standards. The work was carried out under an interagency agreement between the Department of Commerce and the Environmental Protection Agency dated June, 1972.

A. Scope of Report

The report assesses the capability and costs of various methods of determining the concentration of trace elements (< 100 ppm) in the following basic sample matrices: fly ash, coal, oil, ores, minerals, metals, alloys, organometallics, incinerator particulates, slurry streams, and feeds to and from sedimentation processes. As the occasion presents itself, additional matrices may be mentioned, as water, sediments and coagulates.

The trace elements of analytical interest include: mercury, beryllium, cadmium, arsenic, vanadium, manganese, nickel, antimony, chromium, zinc, copper, lead, selenium, boron, fluorine, lithium, silver, tin, iron, strontium, sodium, potassium, calcium, silicon, magnesium, uranium, and thorium. In this listing the elements may be considered as major or minor constituents according to their relative concentrations in the matrix materials, but most of the attention will be directed toward elements present at or below the 100 ppm (100 μg/g) level.

The analytical methods included in this review embrace nuclear methods, mass spectrometric methods, x-ray, optical, and electrometric methods of analysis, specifically:

1. Nuclear methods

2. Spark source mass spectrometry

3. X-ray fluorescence and electron microprobe spectrometry

4. Atomic absorption spectrometry

5. Absorption spectrophotometry

6. Atomic emission spectroscopy

7. Voltammetry (polarography) and potentiometry (ion-selective electrodes)

The methods considered are those which are capable of rapidly and accurately determining trace elements in a variety of materials with a minimum of sample manipulation. Analytical methods requiring long and careful sample processing such as isotope-dilution mass spectrometry have not been included in this survey because of their prohibitively high labor cost and slow accumulation of analytical data. For this same reason, wet chemical procedures are considered only as they are involved with instrumental methods such as spectrophotometry.

The performance of the analytical methods is considered from the viewpoint of their capability to carry out the required trace element determinations on the matrices of interest, at a reasonable cost. The parameters of interest include:

1. Instrumentation requirement

2. Detection limit

3. Accuracy
4. Sample preparation
5. Sample size
6. Manpower skills requirement
7. Cost per analysis

The performance parameters are listed in no special order. The information for each analytical method is taken from the literature wherever possible, and supplemented from the personal experience of the NBS staff members in other cases where literature references are not available. These performance parameters provide guidelines for comparing the various analytical methods but they do not contain sufficient information to permit a decision to be made that one method is superior to another in a specific application.

B. Organization of Report

The report is divided into chapters describing the analytical methods under consideration. The chapters contain bibliographies citing general sources of information and specific references keyed to the elements of interest in the matrices being analyzed. Tables summarizing the analysis of each element according to detection limit, cost, and other performance parameters are included for each method. The accompanying chapter texts provide comments and connecting narrative.

Various indexes are provided to facilitate access to the tabular information pertaining to the determination of each trace element likely to be present in the matrix materials. Details of methods of analysis of specific matrices, or determination of specific elements, or costs of such determinations may be located in the chapter texts, tables, and bibliographies by reference to these indexes or to the Table of Contents.

The sample matrices are grouped differently in each chapter depending on the common characteristics of importance to each analytical method. For example, one analytical method may group the matrices according to their silica content or their solubility in mineral acids, while another method may find a common denominator to be the organic content. The table headings provide entry into the analytical information and the references.

Costs are listed in the tables as the cost of analyzing a single sample. In some cases each element is the sole constituent being determined, as in atomic absorption spectrometry; and in other cases each element is considered to be one of a group of elements being determined sequentially, as with x-ray fluorescence, or simultaneously on the same sample, as with spark source mass spectrometry. The costs of trace element determinations will generally fall between the two extremes of low-cost multi-element survey methods and high-cost single-element determinations. Also, the cost per sample for large numbers of routine determinations can be expected to be less than indicated in the tables. Accordingly, the tabulated values should be considered as guidelines to maximum reasonable costs when the analyses are done by experienced, trained analysts.

Tables in each chapter list performance parameters for each method of analysis according to matrices and trace elements of interest. Where possible, information is provided on sample sizes required, analytical accuracies expected, and costs of determining elements present at concentrations about 1, 10, or 100 ppm. Some methods of analysis not particularly suited for trace determinations (e.g. x-ray fluorescence) are described for element concentrations considerably above 100 ppm in order to present a complete picture of the methods' capabilities.

The tabulated information and supporting references are presented without judgments as to the relative merits of the various analytical instruments and procedures. Decisions regarding the suitability of alternative methods for trace element determinations should be based on experiences with real samples.

2. TRACE ANALYSIS OF REAL SAMPLES

A. Materials Balances

An assessment of the environmental impact of an industrial process or subprocess requires analytical data of several kinds. Figure 1 is a flow diagram showing the different chemical analyses that might be used to monitor the material flow in and out of a typical process. Ores and scrap metals are analyzed before they are smelted in a blast furnace, and the commercial metals and crude intermediates are analyzed as products. The effluent gases, solids, and liquids are analyzed before being recycled, recovered as by-products, or treated and released to the environment as wastes. As indicated in Figure 1, these data might be expected to indicate a materials balance because all of the inputs and outputs are being analyzed.

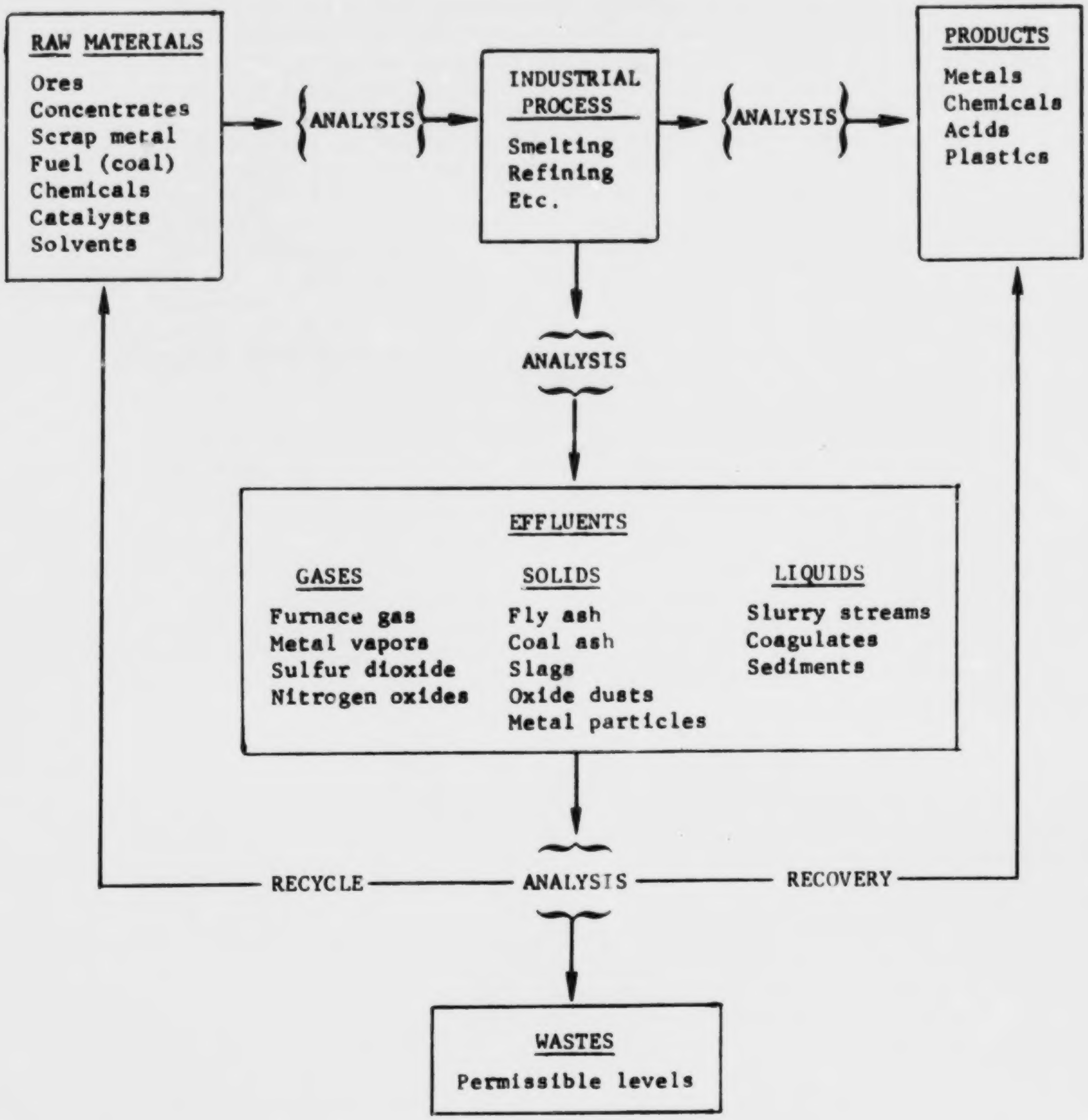
RAW MATERIALS
Ores
Concentrates
Scrap metal
Fuel (coal)
Chemicals
Catalysts
Solvents
ANALYSIS
INDUSTRIAL PROCESS
Smelting
Refining
Etc.
ANALYSIS
PRODUCTS
Metals
Chemicals
Acids
Plastics
ANALYSIS
EFFLUENTS
GASES
Furnace gas
Metal vapors
Sulfur dioxide
Nitrogen oxides
SOLIDS
Fly ash
Coal ash
Slags
Oxide dusts
Metal particles
LIQUIDS
Slurry streams
Coagulates
Sediments
RECYCLE
ANALYSIS
RECOVERY
WASTES
Permissible levels

Figure 1. Applications of trace element analysis to monitoring materials, process streams, and effluents of a typical industrial process.

However, achieving a complete materials balance among all of the trace constituents may be a difficult undertaking, especially if trace elements interchange between process materials and walls of pipes and vessels, or if there are minute losses or additions from the environment (i.e. contamination). Many engineers would be pleased with a product purity of 99.9 percent, but the analytical chemist sees 1,000 ppm of other constituents in this product. This difference in outlook between the engineering viewpoint and the chemist viewpoint is crucial to an understanding of the relative merits of the different analytical methods. The materials balance which is complete to 100.0 percent from an engineering viewpoint is not good enough to account for trace elements; it must be complete to 100.0000 percent to account for a 1 ppm constituent.

For a material balance of trace constituents to be reliable, the analyses must be not only precise, they must above all be accurate. A small error in the analysis of a major component of the raw material could lead to a serious error of judgment regarding the need for, or the reliability of the analyses in the final products, or waste products, or emissions. Accurate measurements are best ensured when dependable, evaluated methods of analysis are used, and requisite calibrations made with reference materials are interspersed in the course of the analyses to provide quality control.

B. Matrices of Interest

Trace element analyses can be carried out routinely after suitable procedures have been established and the requisite instrumentation installed. The materials under consideration for trace determination may be thought of primarily among the products and effluents if the main concern is environmental contamination; however, ores, fuels, and other process inputs should be included in the interest of a suitable materials balance. The diversity of materials to be analyzed is demonstrated in this listing of matrices which may contain trace elements of environmental importance:

1. Raw materials such as ores, concentrates, scrap metals, coal and coke, chemicals, catalysts.

2. Products and intermediates including commercial metal, slags, sinters, blister metal, and bullion.

3. Gaseous emissions including acid mists, fly ash and other particulates as metallic and metal-oxide dusts, partly burned fuels.

4. Process waste waters including coagulates, sediments, and sludges produced in the course of upgrading effluents for pollution control.

5. Plant working environment including dusts, filters, water and solvents, lubricating oils, vapors from molten metals.

The number and variety of sample materials and their expected complexity and inhomogeneity can give rise to difficult problems in sample collection and analysis. Just as chemical analysis is a specialized field, the sampling of process streams requires sophisticated planning by engineering specialists to assure that the samples are representative of the materials of interest. Since such an assurance is vital to the success of the trace element determinations, some of the problems encountered in sampling will be discussed.

C. Sampling

One of the most important considerations in chemical analysis is the assurance that the samples in the laboratory are truly representative of the bulk materials from which they have been taken; and this is especially true in the case of trace determinations. It is obvious that analysis can give information only about the particular samples in the laboratory. If these are not the same composition as the slags, sediments, process streams, etc. which they purport to represent, then the chemical results can have no value whatever and may even be misleading. Obtaining a representative sample may not be a simple matter. The matrix materials are typically inhomogeneous, consisting of two or more poorly mixed phases most of the time. The trace element compositions may be changing continually since they depend upon the interaction of a great many process variables, e.g. impurities in the ores, process side reactions, transfer of material to or from vessel walls and pipes, loss of volatile elements during roasting, transfer of material to or from filters; all these may affect the trace element content of the matrix materials.

Sampling of heterogeneous combinations of liquids, solids, and gases such as gas-borne particulates, mists, slurries, and sludges requires careful planning. It is essential that the number and selection of samples taken for analysis be such as to assure that all the trace elements present in the matrices are represented in their correct concentrations. The problems encountered in sampling process streams for trace constituents may arise from such sources as (1) the inhomogeneity of the matrix materials, (2) composition changes with time or some process variable, (3) sample alteration during sampling and transport to the receiver, (4) sample alteration within the receiver, and (5) inefficient collectors which do not capture 100 percent of the trace elements along with the samples. Collection of representative samples from process streams may require the combined efforts of engineering specialists in stream analysis, fluid mechanics, chemical reactions, corrosion, and materials separation to name a few disciplines.

It is important to understand why the sampling is being done, what streams and what phases in the streams are to be sampled, where are the best places to sample, when are the best times to sample, how big a sample to take, how long a sampling time, how to collect and retain all the trace elements. [1]

An often overlooked factor in sampling is the detailed and unambiguous identification of analytical samples. Such vital information as date, time, and location of sampling should be recorded. Other pertinent information such as process parameters at the time of sampling, and even the then-existing environmental conditions may be of importance in many cases to a proper interpretation of the analytical data. The name of the person taking the sample, and reference to the notebook or log sheet should also be indicated. All of these matters assume special importance when legal considerations may be involved.

The analytical chemist ordinarily requires only a part of the sample collected. In this event it is imperative that the portion used for analysis be representative of the sample submitted to the laboratory. Trained analytical chemists are aware of such matters, but the availability of analytical instruments that can be used by laymen prompts this note of caution. Even the trained analyst needs to be reminded to properly identify each sample analyzed and document the experimental conditions used. Calibration procedures and quality control measures should be recorded to provide authentication which might be needed at a later date. In some cases a bank of analyzed samples may be retained for further analysis, for verification, for later reference, or for other purposes.

Since the analytical chemist has no control over the samples before they reach the laboratory, the forthcoming discussions of instrumental chemical analysis will assume that the samples presented for analysis have been obtained knowledgeably and are free from losses or outside contamination.

D. Choice of Analytical Method

Although the performance parameters which comprise the bulk of the tabulated information seem to provide a basis for comparison of the relative merits of the alternative methods of analysis, it is possible that such a comparison might have little application to the real world of dirty samples and fallible people. In fact, it may be generally impossible to decide a priori that one method will be superior to another in a specific situation, because of the numerous subjective considerations which cannot be accounted for, in a report of this type. The rationale behind the choice of performance parameters establishes the general acceptability of the analytical methods according to accepted standards of accuracy, detection limits, analytical costs, etc. However, there are many opportunities for experimental error and operator bias which may be caused by the effects of the matrix constituents themselves on the analyses, or by differences in reagents and standards used by the various laboratories; or by the ability of analysts to obtain the optimum results with their instruments and operating procedures; or the extent to which the samples reflect the actual bulk matrix compositions, and so on.

The "best" methods of analysis will be those that perform most reliably in the actual analysis of real samples. Such methods probably cannot be identified until a body of analytical results is accumulated. It is realistic to acknowledge that the "best" methods often are those with which the laboratories have the greatest experience. New and unfamiliar analytical methods require an investigative or break-in period whose cost must either be recovered through volume analyses or considered a worthwhile investment in improved technological capability, before such new methods are adopted. The value of this report and other compendiums of analytical methods [2] lies in their utility as guidelines to show what others have done to solve similar problems in trace analysis. Judgments as to what can be done in specific situations should be based on careful observation of test results.

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[2] Pinta, M., "Detection and Determination of Trace Elements," original edition Dunod, Paris (1962) in French. English edition, Ann Arbor Science Publishers, Ann Arbor, Michigan, fourth printing (1972).

CHAPTER 2

NUCLEAR METHODS

Donald A. Becker

1. INTRODUCTION

Nuclear methods of analysis have for many years been deeply involved in the analysis of trace levels of numerous elements in a wide variety of sample matrices. This chapter lists the capabilities of the various nuclear methods and provides references to demonstrate their feasibility. However, since most nuclear techniques depend more on the specific elements present in the sample, rather than the broad category of matrix type, no specific matrix differentiation has been made in the accompanying table. Some discussions of the individual matrices of interest are included under Section 3.

2. NUCLEAR METHODS

The broad category of nuclear methods includes almost all methods which depend upon the measurement of a radioisotope resulting from an irradiation process. A brief description of the more important methods presently in use follows:

A. AS - Activation Spectrometry (Instrumental Neutron Activation Analysis)

This is the method of choice if sufficient sensitivity and specificity are available. In this technique, a sample is irradiated in a neutron source (usually a nuclear reactor, to obtain the required sensitivity) for a period of time, and, after withdrawing the sample, the resulting induced radioactivity is observed. This radioactivity is usually detected and quantitated using a high resolution lithium-drifted germanium semiconductor detector [Ge(Li)] for greatest specificity. In this technique, each radioisotope may be uniquely identified through the observation of a.) its gamma-ray energy; b.) its half-life; and c.) its peak ratios (if it has two or more gamma-ray peaks). It is limited primarily by the total radioactivity induced in the sample under evaluation, and often long decay times are required for many elements. However, it is usually possible to determine many elements simultaneously with one or two irradiations and 2 or 4 counts of a particular sample and associated standards.

B. NAA - Neutron Activation Analysis

This method is similar to the previous technique, except that a radiochemical separation can be employed after irradiation, but before measuring the radioactivity. This separation, if done competently, can remove all or most of the interfering radioactivities while retaining all or a known portion of the radioisotope(s) of interest. Thus, while additional effort is required for the separation, the resulting product is one of a few radioisotopes of interest with little or no other interfering radioactivities. Thus, it is usually possible to obtain maximum sensitivity along with high precision and accuracy with this technique.

C. FNAA - Fast Neutron Activation Analysis

This is another method of activation analysis in which fast neutrons are used as the irradiation source. This fast neutron source could be a Cockcroft-Walton neutron generator producing 14 MeV neutrons, another type of particle accelerator used for generating fast neutrons, or a radioisotope source such as californium-252, producing neutrons by spontaneous fission with energies peaking around 2-3 MeV. However, this technique is seldom used for trace analysis due to a lack of sensitivity caused primarily by the relatively low fast neutron fluxes currently available.

D. CPAA - Charged Particle Activation Analysis

This method of activation analysis depends upon the use of radioisotopes produced in the sample by a charged particle beam from accelerators such as a tandem-Van de Graaf or a cyclotron. This method has the capability of detecting several elements difficult to determine by other nuclear methods, and thus has found some limited usefulness. The technique is limited to a great extent by the nature of its irradiation beam, since it can penetrate to only a few micronmeters depth in the sample. Thus, while found to have great applicability in the field of surface analysis, it is quite limited for the types of samples under consideration here.

E. PAA - Photon Activation Analysis

The method of photon activation analysis utilizes the bremsstrahlung radiation produced by the deceleration of very energetic electrons in a high Z material. One excellent source of such radiation is the Linear Electron Accelerator, or LINAC. These high energy photons are very penetrating, thus producing an irradiation source quite useful for several elements, especially those which are difficult to determine by neutron activation analysis. This technique also uses a Ge(Li) detector system for counting, and can also have a radiochemical separation step included in the analysis. Two of the important disadvantages, however, include the lack of generally available LINAC's and the general similarity of gamma-ray energies of the radioisotopes produced by the prevalent (γ,n) nuclear reactions (usually positron emitters).

F. NTT - Nuclear Track Technique

The nuclear track technique makes use of the fission or alpha particle decay of a nucleus undergoing neutron bombardment. If a smooth surface of the sample or a solution of the sample is placed in intimate contact with a special type of plastic, then irradiated (usually with thermal neutrons), several elements produce a track in the plastic which can then be chemically etched and counted microscopically. At present, of the elements of interest here, only boron and uranium can be determined by this technique.

G. IDA - Isotope Dilution Analysis

A number of elements can also be determined using the technique of isotope dilution analysis. This heading includes both isotope dilution analysis and its related technique of substoichiometric isotope dilution analysis. In these methods, a radioisotope of the element of interest with known specific activity is added to the sample, after which all or a portion of the "diluted" element is separated from the sample. The changed specific activity of the separated radioisotope allows the calculation of the concentration of the element in the sample. This technique is listed in table 1 as a secondary method for several elements.[1]

3. ANALYTICAL APPLICATION TO SPECIFIC MATERIALS

The applicability of nuclear methods for the analysis of fly ash, coal, oil, ores, minerals, metals, alloys, organometallics, incinerator particulates, slurry streams, feeds to/from flotation processes, and sediments in flotation processes has been investigated. It does not seem to be feasible to consider each of these materials separately for all of the elements of interest. Very few papers have been published for these materials even though these methods, especially neutron activation analysis, are eminently suitable for most of the elements in all of the matrices. Thus, only an overview of the different sample matrices will be given here, with some references to specific publications, if available. It must also be remembered, however, that dissolution of the sample after irradiation, with an appropriate radiochemical separation of the element of interest, will yield a determination which is essentially similar for all sample matrices. This is not only possible, but is currently being done in the NBS laboratory as well as many other activation analysis laboratories. This fact, coupled with the ability to verify radioisotopic purity by at least two and possibly three different parameters (i.e., gamma-ray energy, half-life, and peak-ratios) enables reliable analytical data to be obtained for most elements for almost all types of samples.

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[1] This is not to be confused with Isotope Dilution Mass Spectrometry which uses enriched stable isotopes as tracers, rather than radioactive isotopes.

A. Fly Ash

The primary difficulty in the analysis of fly ash is the high radioactivity level resulting from neutron irradiation. However, since impurity levels are also generally high, the sensitivity loss should not be a problem. Many elements can be determined non-destructively, however, the shortlived radioisotopes (e.g., calcium, magnesium, vanadium) may be impossible to detect at low concentrations. This material can be dissolved in acid mixtures and the element(s) of interest separated, with some increase in cost but with much improved sensitivity. Unfortunately, very little analytical data have been published on fly ash.

B. Coal

This matrix is elementally similar to biological materials, and thus can be tentatively considered in terms of neutron activation analysis results on human tissue (86) and botanical samples (87). In the first publication 30 elements were determined in individual samples by radiochemical separations and gamma-ray spectrometry (86). In the second publication 15 elements were determined non-destructively in samples of dried kale leaves. Again, sample dissolution is simple and separations can be performed to improve the sensitivity and specificity for individual elements or small groups of elements. Many additional activation analysis references are available for trace element analyses in biomedical samples (90,91,92), but only one was found in which a coal was the sample matrix (68).

C. Oil

The activation analysis of oil samples has been demonstrated several times, notably the determination of 13 trace elements by AS in crude petroleum (81), and the systematic determination of 11 trace elements in crude oils, distillation fractions, asphalts, etc., by NAA with radiochemical separations (88). In this latter paper, comparisons were made for some elements with results by other analytical techniques, and precisions of ±10 percent claimed for the NAA results. Additional papers present work on the characterization of marine oil pollution sources by AS (89,97).

D. Ores and Minerals

The activation analysis technique has been applied to large numbers of geological type samples (93,94,95) and to some ore and ore processing product samples (96). In one case, a single sample weighing less than one gram was analyzed by neutron activation with radiochemical separations, and 39 elements were determined with precisions of better than ±5 percent claimed for over half of the elements (95). In a second situation, a neutron generator (FNAA) was used to activate samples and rapid, nondestructive analyses were made for several elements with sensitivities of about 1 mg (96). In an ore and mineral type of sample, the capability of any nondestructive activation technique depends to a significant extent on the concentration of other elements in the matrix. Thus, some preliminary evaluation will usually have to be made before an established analytical procedure can be applied.

E. Metals and Alloys

Much analytical data have been published on the activation analysis of trace elements in metals and alloys. Several particularly useful references other than those from table 2 are included here (98,99,100). The ease of analysis depends significantly on the activation of the matrix material. Thus, much of the work reported in the literature has been made on sample matrices which are relatively easy, such as aluminum, iron, lead and bismuth. Metals and alloys which activate strongly (such as manganese, copper, gold, antimony) or fission under neutron irradiation (such as uranium or thorium) are much more difficult to analyze for trace element concentrations.

F. Organometallics

Organometallics have been analyzed by activation analysis for major constituents (101,102), but not often for trace contaminants. This is most likely due to a lack of interest in trace element information, since thermal neutron activation analysis would seem to be especially suited to this type of sample. However, some restrictions might be found necessary for the irradiation of very volatile liquids or explosive compounds in a nuclear reactor.

G. Incinerator Particulates

The characteristics of this type of sample would probably be somewhere between fly ash and coal. No particular problems are foreseen that were not already mentioned, but no publications are available which specifically treat this material.

H. Slurry Streams, Feeds to/from Flotation Processes, and Sediments in Flotation Processes

These sample types are grouped together because there is so little published information on their analysis by nuclear methods. The only references that could be found were two papers, one previously mentioned under ores and minerals (96), plus one additional paper on the use of isotopic neutron sources for process control in the metallurgical industry (103). Again, most of the sample types included here would appear to be very suitable to at least one of the activation analysis methods.

4. RESULTS AND DISCUSSION

The results of this survey of the analysis of environmental materials by nuclear methods are found in table 1. Each element is listed along with pertinent information concerning its determination. As discussed in the introduction, no further breakdown of the data by sample type will be made; general comments can be found in Section 3 of this chapter.

In the explanation of table 1, each column will be commented upon here. For the second, third and fourth columns, (TECHNIQUE USED, ACTIVATION EQUIPMENT, and DETECTION EQUIPMENT, respectively) the definitions can be found at the bottom of the table, and are discussed here and elsewhere.

The instrumentation required for most of the activation procedures listed in table 1 are first, an irradiation source (for AS and NAA, usually a high flux nuclear reactor) or access to one, and second, a pulse height analyzer and high resolution lithium-drifted germanium detector system for detecting and quantifying the induced radioactivites resulting from the irradiation. The activation analysis technique has the substantial advantage over most other trace analytical techniques in that after the sample has been irradiated (i.e., the trace element of interest has been made radioactive) normal contamination problems no longer exist. In fact, when radiochemical separations are used usually macro quantities (10-20 mg) of the element of interest are added to the sample as carrier to minimize separation and adsorption problems. Thus, to retain this advantage, handling and manipulation of the sample before irradiation, (preconcentration, dissolution, etc.) should be kept to a minimum.

Column 5, PREPARATION TIME, is an estimate of the time required for preparation of a sample for analysis. This time does not include the time necessary for counting a sample or calculation of the results, nor does it include the time required for dissolving the sample or for a chemical separation, should that be required. However, such factors are considered in estimating the cost of an analysis.

Column 6 contains the estimated DETECTION LIMIT, in micrograms. Most of the values for AS and NAA have been obtained from published compilations of experimental sensitivity values (104,105). In all cases the value quoted is for the "interference free" situation, using irradiation time of a few hours at a thermal neutron flux of 5×10^{13}n.cm^{-2} sec^{-1}. Where necessary, corrections have been made for counting with a Ge(Li) detector system. These detection limits are realistic, however, especially when employing an effective radiochemical separation to remove any interfering radioactivities from the sample. In fact, the listed detection limit can often be exceeded when specialized counting equipment is used. For instance, even though the listed detection limit for sodium in table 1 is 10^{-3} μg, as little as 4×10^{-6} μg of sodium has been determined with a precision of better than ±10 percent, using a β-γ-γ sum-coincidence spectrometer (36,101).

In column 7, the estimated SAMPLE SIZE (grams) has been listed. This sample size is very flexible for neutron activation analysis and photon activation analysis, although less so for the other nuclear techniques. Samples have been analyzed which range from a few micrograms to tens of grams. However, general sampling considerations limit the sample size to more than 10 mg, while potential self-shielding effects usually limit the sample size to a gram or less.

In column 8, the MANPOWER SKILL LEVEL is assumed to be that of a skilled technician for the AS determinations. This has been shown to be true in a number of laboratories, providing the assumption in the next column is true, that an established analytical procedure is available. To provide that procedure, usually a scientist is required. Also, in many cases where a technician is indicated, a chemist will often be necessary if a radiochemical separation is required. In the table, a chemist is listed whenever special procedures are indicated.

In column 9, the COST PER ANALYSIS is estimated on the basis that an established analytical procedure is available, and that at least 100 samples are to be analyzed. Thus, the values given are for routine analyses, rather than special research type analyses.

In column 10, the SELECTIVITY has been evaluated on the basis of ease of determination by the primary nuclear analytical method. In the case of AS, this is a function of the gamma-ray energy, the half-life, and the general ability of the technique to successfully determine the element nondestructively in a variety of sample types. If a rapid and simple radiochemical separation would be very effective, this may also have been taken into consideration.

Column 11, COMMENTS, includes the evaluation of half-life, decay time, and/or radiochemical separations on sensitivity and specificity, and also lists the alternate nuclear method(s) of analysis for that element along with the pertinent reference(s).

Table 2 contains a listing of references for each individual element in a variety of matrices, often by a number of different nuclear methods. No attempt has been made to be exhaustive, but rather the aim has been to illustrate the analytical determination of that specific element.

No report on an analytical technique would be complete without a few comments on the potential errors and biases involved. These areas have been discussed extensively in the literature and so will not be further discussed here (106,107, 108). It is sufficient to say that the uncertainties involved are well understood, so that with these techniques levels of accuracy and precision of ±5 percent are possible in many cases, and ±25 percent in almost all cases, in capable laboratories.

In conclusion, the various nuclear techniques of analysis have been shown to be capable of the determination of the elements listed in many sample matrices. These techniques, especially neutron activation analysis, activation spectrometry, and photon activation analysis, should be very useful in the analysis of trace elements in environmental samples.

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Table 1. Trace Elements in Environmental Materials

Element Determined	Tech.[a] Used	Activation[b] Equip.	Detection[c] Equip.	Prep'n Time	Detection[d] Limit(µg)	Sample Size(g)	Manpower[e] Skill Level	Cost Per Analysis[f]	Selectivity (Non-dest.)	Comments[g]
Mercury	AS	REACT	PHA-Ge	15 m	10^{-3}	.01-1.0	TECH	$50-100	Good	Chem. Sepn.++; Also: IDA (9)
Beryllium	CPAA	TVDG	PHA-NaI	30 m	1	<0.1	CHEM	100-200	Poor	Also: Photoneutron Tech(20,23,70); AS (40)
Cadmium	AS	REACT	PHA-Ge	15 m	10^{-2}	.01-1.0	TECH	50-100	Good	Often requires Chem. Sepn.; Also:FNAA (29)
Arsenic	AS	REACT	PHA-Ge	15 m	10^{-3}	.01-1.0	TECH	50-100	V. Good	Chem. Sepn.+
Vanadium	AS	REACT	PHA-Ge	15 m	10^{-3}	.01-1.0	TECH	50-100	V. Good	Short half-life
Manganese	AS	REACT	PHA-Ge	15 m	10^{-3}	.01-1.0	TECH	50-100	Exc.	
Nickel	AS	REACT	PHA-Ge	15 m	10^{-3}	.01-1.0	TECH	50-100	Good	Chem. Sepn.++
Antimony	AS	REACT	PHA-Ge	15 m	10^{-4}	.01-1.0	TECH	50-100	V. Good	Also: IDA (7)
Chromium	AS	REACT	PHA-Ge	15 m	10^{-2}	.01-1.0	TECH	50-100	Good	Often requires long decay time or Chem. Sepn.
Zinc	AS	REACT	PHA-Ge	15 m	10^{-2}	.01-1.0	TECH	50-100	V. Good	Either of two isotopes can be used; Also: IDA (9)
Copper	AS	REACT	PHA-Ge	15 m	10^{-3}	.01-1.0	TECH	50-100	Good	Chem. Sepn. ++; Also IDA (8,13)
Lead	PAA	LINAC	PHA-Ge	30 m	5	.01-1.0	TECH	100-200	Good	Chem. Sepn. ++; Also: AS (40)
Selenium	AS	REACT	PHA-Ge	15 m	10^{-2}	.01-1.0	TECH	50-100	Good	Often requires long decay time
Boron	NTT	REACT	SPEC	30 m	10^{-1}	.001-.1	TECH	100-300	--	Also: AS (40); CPAA (24)
Fluorine	AS	REACT	PHA-Ge	15 m	10^{-2}	.01-1.0	TECH	50-100	V. Good	Short half-life; Also CPAA (24); PAA (33)
Lithium	AS	REACT	SPEC	30 m	10^{-3}	.01-1.0	CHEM	100-300	Fair	V. short half-life, uses reactor pulse; Also: Secondary nuclear reaction (64)
Silver	AS	REACT	PHA-Ge	15 m	10^{-3}	.01-1.0	TECH	50-100	Good	Can also use very short half-life isotope (2)
Tin	AS	REACT	PHA-Ge	15 m	10^{-2}	.01-1.0	TECH	50-100	Fair	Requires long decay or Chem. Sepn.
Iron	AS	REACT	PHA-Ge	15 m	1	.01-1.0	TECH	50-100	V. Good	
Strontium	NAA	REACT	PHA-Ge	30 m	10^{-1}	.01-1.0	CHEM	100-200	--	Requires Chem. Sepn.; Also CPAA (41)
Sodium	AS	REACT	PHA-Ge	15 m	10^{-3}	.01-1.0	TECH	50-100	Exc.	
Potassium	AS	REACT	PHA-Ge	15 m	10^{-3}	.01-1.0	TECH	50-100	V. Good	
Calcium	AS	REACT	PHA-Ge	15 m	10^{-1}	.01-1.0	TECH	50-100	Exc	Short half-life; Also: CPAA (39)
Silicon	NAA	REACT	PHA-Ge	30 m	1	.01-1.0	CHEM	100-200	--	Requires Chem.Sepn.; Also: FNAA (33)
Magnesium	AS	REACT	PHA-Ge	15 m	1	.01-1.0	TECH	50-100	Good	Short half-life; Also: FNAA (29)
Uranium	AS	REACT	PHA-Ge	15 m	10^{-2}	.01-1.0	TECH	50-100	Good	Chem.Sepn.++; Also: NTT (34); Delayed neutron (50
Thorium	AS	REACT	PHA-Ge	15 m	10^{-2}	.01-1.0	TECH	50-100	Good	Also: Delayed neutron counting (50)

[a] AS = Activation spectrometry (Instrumental neutron activation analysis); NAA = Neutron activation analysis; FNAA = Fast neutron activation analysis; CPAA = Charged particle activation analysis; PAA - Photon activation analysis; NTT = Nuclear track technique; IDA = Isotope dilution analysis

[b] REACT = Nuclear reactor; TVDG = Tandem Van de Graaf accelerator; LINAC = Linear electron accelerator

[c] PHA Ge = Pulse height analyzer with high resolution germanium gamma-ray detector; PHA-NaI = PHA with sodium iodide detector; SPEC = Special counting techniques (see references).

[d] Detection limits are micrograms of the element, for the interference-free situation; see text.

[e] TECH = skilled technician; CHEM = trained analytical chemist

[f] Estimated on the basis of large (>100) numbers of samples, using an established analytical procedure.

[g] CHEM SEPN + = Significantly improved determination with simple chemical separation; CHEM SEPN ++ = greatly improved determination with simple chemical separation; for explanation of other techniques used, see a.

Table 2
Element Index to References
Nuclear Methods

Element	References
Mercury	9,16,47,67,68,69,81
Beryllium	20,22,23,24,48,70
Cadmium	17,26,29,67,71
Arsenic	29,30,57,67,75,76,81
Vanadium	29,46,57,58,80
Manganese	3,14,29,65,76
Nickel	31,45,77,81
Antimony	7,28,29,76,81
Chromium	15,27,29,32,59,66,77,81
Zinc	9,14,27,29,32,60,61,65,67,76,77,81
Copper	8,13,14,18,27,29,62,65,76,77
Lead	42,48
Selenium	44,63,67,81,82
Boron	24,34,48
Fluorine	24,33,48
Lithium	38,48,64,74
Silver	1,2,29,37,77,83,84
Tin	29,30,56,81
Iron	10,14,40,66,76,77,81
Strontium	29,41,54,55
Sodium	19,29,36,65
Potassium	25,27,29,85
Calcium	6,29,39
Silicon	52,53,77,78
Magnesium	29,43,78
Uranium	4,5,25,34,35,50,51,74,79,81
Thorium	25,49,50,72,73,74

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CHAPTER 3

SPARK SOURCE MASS SPECTROMETRY

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1. INTRODUCTION

In spark source mass spectrometric (SSMS) analysis, samples are introduced as solid "electrodes" into the source chamber which is evacuated to a pressure of $1\text{x}10^{-7}$ to $1\text{x}10^{-8}$ torr[1]. Ions are produced from a pair of sample electrodes by imposing a pulsed radiofrequency voltage of 20 to 80 keV between them. The spark produced vaporizes and ionizes all elements in a small volume of the sample with each pulse. The high energy available in the spark results in the production of multiply charged as well as singly charged ions of all elements. The +1 ions, however, are the most abundant species with a decrease in abundance with each increasing charge (i.e. $Fe^{+1}>Fe^{+2}>Fe^{+3}$, etc.). The ions are accelerated by a 24 kV D.C. potential and pass through an electrostatic sector and then a magnetic sector. The ions are resolved into individual beams in the magnetic sector and dispersed according to their mass to charge ratio. A photographic plate at the exit of the magnet simultaneously detects all elements from Li (mass 7) to U (mass 238) on each exposure. By making a graded series of exposures covering 5 to 6 orders of magnitude, it is possible to determine elements present from the ppb level up to the 100 percent level.

Recently instruments have been produced which have electronic detection as well as photographic detection. These instruments use an ion multiplier to measure ion currents of a single mass line at a time. The full mass range is covered by scanning the ions of the individual lines sequentially across the ion multiplier (by changing the magnetic field strength).

Spark source mass spectrometry is ideally suited to survey an unknown sample for all possible elements from major constituents to those present at the ppb level. The spark source has no inherent "blind spots" for any element and detects all elements with approximately the same sensitivity. Under optimum conditions a detection limit of a few ppb can be obtained for all elements while consuming as little as 10 to 100 mg of sample. This high absolute sensitivity makes the technique applicable to both the analysis of low levels of concentration and the analysis of small samples (such as particulates from a low-volume air sample).

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[1] 1 torr = 133 Pascals.

A. Interferences

Although the SSMS can potentially detect all elements, there will be interferences present which may hinder or prevent the analysis of some elements in real life samples. There are two main sources of possible interferences, the +2, +3, etc. multiply charged ions and molecular ions (hydrocarbons, metal dimers, oxides, etc.) having the same nominal mass to charge ratio as the singly charged line of the element being determined.

Control of experimental conditions and proper plate interpretation techniques minimize the number of potential interferences. An experienced SSMS operator is not likely to misidentify the interference as an element. The existence of actual interferences and the concentration level where the interference starts will depend on what other elements are present in the sample and their concentrations. The actual sample must be run to determine which elements have interferences (at what concentration levels), however from previous experience we know it will be only a small percentage of the possible elements. In a recent publication in American Laboratory, R. Brown [1] reported the simultaneous determination of from 40 to 60 elements in single samples by SSMS. The sample types ranged from lung tissue and coal dust to fly ash.

B. Sample Requirements

The spark source requires conducting or semiconducting samples for sparking which are stable under the 10^{-7} to 10^{-8} torr vacuums present in the instrument. Powders can be mixed with graphite or silver powder and compressed into electrodes suitable for analysis. Techniques are available to analyze essentially any form of sample from liquids to insulating solids by SSMS, however it is important to note that any sample manipulation will result in some degree of contamination of the sample when analyzing at the sub-ppm level for all possible elements.

The high absolute sensitivity of the spark source requires good sample homogeneity in order for the small volume of sample consumed in the analysis to be representative of the bulk of the sample. Powders used for analysis should be ∿100 mesh size and be well mixed in order to meet this homogeneity requirement.

C. Sensitivity

Modern spark source instruments can obtain 1 ppb detection limits with 1 hour of sample sparking at ∿2000 resolution ($\frac{\text{mass}}{\Delta \text{ mass}}$) using photographic detection. If the instrument has electrical detection, 0.1 ppm detection limits are obtained when scanning the entire mass range in $\sim$10 minutes, Detection limits at the ppb level are obtained from electrical detection when using the peak switching mode (1 to 30 sec integration of each peak), however this mode only allows examination of a limited number of elements in each sample (10 to 20 elements). Both modes of electrical detection are normally operated at a resolution of only 500, making it incapable of resolving any interference involving a line having the same nominal mass as the analytical line being measured.

2. PRECISION OF MEASUREMENTS BY SSMS

The uniformity of the photographic plates used in SSMS analysis limits the precision of measurements to $\sim\pm5$ percent, and this level of precision is usually only obtained in the measurement of the isotopic ratios for an element, provided the ratio is measured within a single exposure. When measurements are made involving the absolute intensities between exposures, (as in most types of analysis) precisions of ±15 to 20 percent are usually obtained. The scanning mode of electronic detection gives precisions of ±10 to 30 percent [2] and in the peak switch mode of electronic detection, precisions can approach ±1 percent [2] under favorable conditions.

3. ACCURACY OF ANALYSIS BY SSMS

The accuracy of a spark source analysis on the other hand will usually depend on the availability of a suitable reference standard with the same composition (same basic matrix). With a good reference standard the obtainable accuracies can equal the precision values just mentioned. The following is a general outline of different approaches to the standards problem:

A. No Standards Used; Concentrations Estimated

It was mentioned previously that the SSMS detects all elements with approximately the same sensitivity. The accepted method of computing results for SSMS analysis when no standard is available is to assume that all elements have the same atomic sensitivity as the matrix and equate relative line intensities to element concentrations. Results calculated in this manner are usually reported to be within a factor of 3 to 10 of the correct result. A study at NBS of 12 Standard Reference Materials (all metals or metal alloys) by SSMS yielded analysis with 75 percent of the computed impurity concentrations within a factor of 3 and 95 percent within a factor of 5 of the certified concentrations.

Although this range in accuracy may not be adequate for the final analysis of a sample, the complete elemental coverage and the sub-ppm detection limits make it the ideal survey technique. An analysis of this type will provide the information necessary to make the decision as to which elements need to be determined more accurately by other techniques.

While an analysis without a standard can be in error by a factor of 3 to 10, it is possible to compare the relative concentrations of impurity elements in different samples to within ±20 percent, providing the basic matrix composition does not change. A significant number of useful SSMS analyses in the past have involved the detection and correlation of relative changes in concentration even though these changes were small compared to the uncertainty in the reported absolute concentration levels.

B. Analysis Using Standard Reference Materials (SRM's)

Many certified SRM's are available from NBS and other sources which can be used as reference standards for SSMS analysis. As long as the major components of the standard and the unknown samples are the same, a single standard is valid for a wide concentration range. (Halliday et al. [3] showed a linear response for gold through five orders of magnitude in a titanium matrix.)

Use of a standard, and careful control of all instrument parameters produce ±15 percent accuracy with the photographic plate detection; ±6 to 8 percent accuracy has been obtained under special conditions [4]. Electrical detection in the scanning mode can yield ±10 to 30 percent accuracy [2] depending on the number of scans, and peak switching ±4 to 7 percent [2,5]. At the lower error levels and low concentrations the uncertainties in the certified standard may be a significant source of error. Unfortunately, most standards will have only 20 to 30 elements certified, these may cover only half of the elements detected in a survey analysis and thus still present a problem.

C. Analysis Using Synthetic Standards

Powdered samples which are normally mixed with graphite (silver, etc.) powder and pressed into electrodes for analysis, and other types of samples can be conveniently compared to synthetic standards prepared in an identical manner. Griffith et al. [6] used this method for determination of rare earths in rare earth oxides, and Nicholls et al. [7] used it for determining elements in geological materials. Accuracies from ±20 to ±5 percent are claimed using photoplate detection. The accuracy of analysis will depend upon the synthetic standard having elements chemically combined in the same way as they are in the sample. Thus, $CrCl_3$ (or $K_2Cr_2O_7$) added to a graphite mix in a known concentration could not serve as a reference standard for the determination of Cr in a ruby powder (mixed with graphite) where the Cr is locked inside the highly refractory Al_2O_3 matrix. It could serve quite adequately, however, for determining Cr in water solutions which were prepared for sparking by evaporation with graphite powder, mixing, and pressing into electrodes.

D. Analysis Using Stable Isotope Dilution

Isotope dilution analysis with the SSMS can provide an absolute method of analysis (requiring no standards) to accuracies of ±5 percent for any element having two or more stable isotopes. With this technique a known amount of an enriched separated isotope (spike) of an element is added to the sample being analyzed; following chemical and physical equilibrium of the "spike" isotope with the natural isotopes of the element, the element is separated from the matrix and the altered isotopic ratio is determined with the SSMS. Only three measured quantities are required to compute a concentration: (1) the sample weight, (2) the amount of separated isotope added and (3) the altered isotopic ratio. In most samples several elements can be determined simultaneously by SSMS isotope dilution, from a single sample treatment. This is the only technique used at NBS for the SSMS analysis of Standard Reference Materials for certification. Elemental concentrations have ranged down to the low ppb level [8,9,10], and to sub-ppb levels [11] for systems amenable to preconcentration.

In all SSMS analysis techniques, other than isotope dilution, the accuracy of an analysis ultimately depends on the ability to run both the sample and reference standard under identical conditions. The sample homogeneity, the gap between sample electrodes during sparking, their alignment with the ion optical axis of the instrument, the voltage of the R.F. spark, plus other operational parameters can affect the absolute intensity of an element line when compared to the total ion current or the intensity of an internal standard element. Although these parameters affect the absolute intensity of an element's lines, they have no measurable effect on the isotope ratio of an element (photographic detection) measured on a single exposure. The precision and accuracy of an analysis by SSMS isotope dilution is therefore limited only by the ±5 percent uniformity of the photographic plate.

4. PROCEDURE FOR ANALYSIS OF MATERIALS

The materials covered by this report can be grouped according to the treatment required to get the samples into forms suitable for sparking in the mass spectrometer. The forms used will, in turn, be controlled by the standardization method (precision and accuracy) desired.

Group I

Coal, oil, organometallics (organic content)

Group II

Fly ash, ores, minerals, incinerator particles, slurry streams, feeds to and from flotation processes, sediments in flotation processes (all inorganic solids [after evaporation of water], nonconducting)

Group III

Metals, alloys (conducting samples which can be run as is, with no treatment other than cutting to size)

A. Group I Matrices

The SSMS has about the same sensitivity for organic compounds as it does for inorganic elements. The ∿2000 resolution normally obtained with photographic detection will completely resolve equal-intensity hydrocarbon and element lines having the same nominal mass. In the presence of a gross excess of hydrocarbons from Group I samples, however, higher resolution would be required to maintain separation of the lines. SSMS instruments now being sold can be adjusted to resolutions of 10,000 and higher, but at the expense of sensitivity. The 500 resolution of the electronic detection mode is incapable of resolving hydrocarbons from elements at the same nominal mass and cannot be used when hydrocarbon lines are present. Coal is presently being run directly [1,12] and after dry ashing. Dry ashing not only permits the use of the higher sensitivity 2000 resolution range, it also preconcentrates the inorganic material being analyzed from 10 to 100-fold. Dry ashing can lose volatile elements such as Hg, Te, Cd, As, etc. If analysis of such elements is desired, a wet ash procedure would be better. Both oils and organometallics can be handled by wet ashing, possibly in sealed tubes or bombs.

B. Group II Matrices

The slurry streams, feeds to and from flotation processes, and sediments in flotation processes require removal of water by drying. In the dry form all of this group could be handled the same way. Direct sparking of these nonconducting materials requires mixing with a conducting powder such as graphite (silver, etc.). Sample grinding may be necessary to obtain the ∿100 mesh size required for sample homogeneity. Geological survey samples could be used as reference standards for some minerals, ores, and materials from the flotation process but certainly not for all of them and not for either fly ash or slurry streams. A synthetic standard mixed with graphite would certainly give better results than estimating concentrations, but the fact that the synthetic standard does not match the physical-chemical form of the actual samples could cause relatively large errors. The problem of producing a synthetic standard identical to a sample could be solved by dissolving all samples in mineral acids (this also applies to Groups I and III). Such solutions could then be exactly duplicated with a synthetic mixture.

C. Group III Matrices (metals and alloys)

No special sample treatment is normally required. Standard Reference Materials are most readily available for these type samples. If a standard is not available or if critical elements have not been certified in the SRM's, the sample can either be dissolved for a comparison to a synthetic standard or analyzed by isotope dilution.

It has been pointed out that to obtain a synthetic standard that is identical to a sample, the sample itself may have to be dissolved. Any such sample processing will introduce contamination of the samples. Dissolution of samples (wet ashing) would normally be done with excess amounts of acids. The problems actually encountered will depend on what elements are to be determined and their concentration levels with respect to the purity and amounts of acids being used for dissolution. In addition, dissolution dilutes the sample and hence reduces sensitivity. However, even if the subsequent precessing involves redrying of the sample, the added acid anions still represent a significant amount of sample dilution. The added anions are even more troublesome as a source of molecular interference when combined with cations. The alkalis and alkaline earths are particularly inclined to combine with anions to form ionized molecular species in the spark source.

Samples starting as water solutions or samples dissolved for purpose of analysis can be handled a number of ways:

1. They can be frozen in a liquid nitrogen cooled "cup" and sparked directly using a high purity counter electrode [13].

2. They can be evaporated to dryness on a high purity substrate and sparked against a high purity counter electrode [14].

3. The solution can be slurried with graphite, evaporated to dryness, mixed, and pressed into electrodes [1].

4. The solution can be "spiked" and analyzed by isotope dilution analysis.

System 3 would be most amenable for use with the "synthetic" reference standard.

5. ANALYSIS BY ISOTOPE DILUTION

Isotope dilution is the most accurate means of analysis available to the SSMS. However, it does not have the element coverage that is available in the direct sparking of a sample. Factors involved in isotope dilution analysis by SSMS are:

1. It applies only to elements with two or more isotopes and cannot be used for gases.

2. The requirement of mixing the spike isotope with the natural element isotopes physically and chemically (both in oxidation states and in chemical form) means that all samples must be put into solution as a minimum treatment.

3. Measurement of an isotope ratio by SSMS requires about 10^{-8} to 10^{-6} grams of an element for consumption in the sparked volume (<10 mg).

4. Item 3 plus problems of interferences in essence require a preconcentration step for any isotope dilution analysis of elements below a few hundred ppm. The preconcentration should include the removal of water, the major (unanalyzed) cations and anions. Since only the isotope ratio is measured for each element, the efficiency of a preconcentration procedure is not important so long as enough material is recovered to measure the ratio. General group separation

procedures such as electrodeposition, anion or cation exchange and solvent extraction have been used in our laboratory for preconcentration. Generally the last step has been electrodeposition onto pure gold wires for sparking. Preconcentration of water and acids [11] is obtained simply by evaporation onto the gold wires used for sparking.

5. Analysis by isotope dilution requires that the measured altered ratio be significantly different from both the natural and "spike" isotopic ratios. A photoplate will give the best accuracy if the final ratio is ∿1 (2 if the natural ratio is 1).

6. Item 5 plus the limited dynamic range of intensity covered by a single exposure on a photoplate restricts the concentration range covered by a single spiking to a factor of ∿10 up or down from the optimum ratio.

7. Our laboratory has not attempted isotope dilution analysis on SRM's above several hundred ppm since other techniques are normally available at NBS which can give better accuracy than the SSMS at these high concentrations. For elements attempted below this concentration, a single group separation technique has enabled successful isotope dilution analysis of approximately half of the elements present in the sample. Six to eight elements are usually determined simultaneously in each sample.

There is a specific application of environmental interest where isotope dilution by SSMS can be both very effective and relatively inexpensive to use. It is the analysis problem of testing a material to see whether it meets certain legal concentration specifications for trace elements (e.g., pollution standards!!). In this situation, the sample would be spiked with the exact amount of spike isotope that gives an altered isotope ratio of 1 at the critical specified concentration. A visual inspection of isotope ratios on the SSMS photoplate would rapidly identify any element that is present in an amount grossly above or below the specification levels. Only those elements whose concentrations are close to meeting or failing specifications would have to be measured with a densitometer. The analysis would give its most reliable results exactly at the critical, specified concentrations. If this technique were applied to the analysis of water supplies, evaporation-preconcentration techniques could give detection limits as low as 0.01 to 0.1 parts per billion on ∿50 ml of water [11].

6. ELEMENT COVERAGE OF SSMS ANALYSIS

All analyses by SSMS will involve the determination of many elements simultaneously from each sample. Since the only "blind" spots in SSMS analysis are generated by the constituents of the sample itself, the sample must be analyzed before it is known which elements cannot be determined. The total number of interferences will be always less than ∿30 percent of all the elements. Table 1 is taken from a recent publication by Brown et al. [1]. He was able to detect over 60 elements in both fly ash and coal samples by SSMS. Table 1 lists all 27 of the desired elements detected in fly ash and 26 of the 27 desired elements found in coal. Overall, for group I, II, and III samples, we can estimate that at least 20 elements of the 27 listed for this report could be determined for each sample; however, the specific elements would not be known until the samples were run. In general, the low mass elements are the ones having most interferences.

Isotope dilution would have the lowest element coverage of any SSMS technique. The NBS laboratory has determined in various sample matrices, 16 of the 27 elements listed. (Hg, Cd, Ni, Sb, Cr, Zn, Cu, Pb, Se, Ag, Sn, Fe, Sr, K, Ca and Mg.) U and Th should also be readily determinable. Experience with NBS SRM samples indicates that about 10 to 12 of the elements can be separated as a group with a single separation procedure and be determined simultaneously by SSMS isotope dilution. One-gram samples would give analyses down to ∿0.1 ppm with accuracies of ±5 to 10 percent at 1 ppm and higher.

7. COST (TIME) OF ANALYSIS BY SSMS

It is assumed that the number of similar samples to be analyzed will be large enough so that the initial set up times can be ignored. These estimates are based on experiences of a one-man laboratory; larger laboratories should be more efficient. Only two examples will be given which represent extremes for cost, coverage and accuracy; (a) an all inclusive survey analysis with estimations of concentrations (factor of 3 to 10) and (b) isotope dilution analysis of a limited number of multi-isotope elements.

1. Survey analysis for all possible elements, no reference standard used, visual interpretation of photographic plate (no densitometry), all samples except possibly oil and organo-metallics.

a. Sample preparation ~1 hour or less.

b. SSMS instrument and photoplate development ~1 hour.

c. Photoplate interpretation ~1 hour.

TOTAL Two to four samples tested for ~60 elements per man day - results ±3 to 10 fold.

2. Isotope dilution analysis. Accurately spiked sample, densitometry of photographic plate, computer calculations of results for all samples.

a. Sample dissolution, spiking, preconcentration ~1/2 day.

b. SSMS instrument time and plate development ~1 hour.

c. Densitometry of plate and computation of results ~3 hours.

TOTAL One sample for 8 to 12 elements per man day - results to ±5 to 10 percent accuracy.

8. CONCLUSION

There are two types of applications where the SSMS can be clearly superior to any other single analytical method.

1. To survey a completely "unknown" sample for all possible trace elements to concentrations well below 1 ppm. A direct sparking without standards (x3 to x10 accuracy) would give an analysis adequate for making decisions as to which elements were at high enough concentrations to require an accurate analysis. This SSMS survey analysis would also contain enough information to permit decisions to be made as to which analytical techniques should be used for each element, based on the concentration levels sought and possible interferences from other elements.

2. Use of SSMS isotope dilution to test environmental samples for compliance to preset standards of acceptable concentration levels for toxic elements (many elements simultaneously).

Such samples can be spiked so that each element being tested gives an altered isotope ratio of 1 (or 2 for some elements) at its critical level. In this case rapid visual plate interpretation would identify all elements which grossly pass or fail. Only elements near the critical concentrations would require the more precise densitometry data, and these results would be most reliable at the specified concentration. Easily preconcentrated samples, such as drinking water supplies, could have detection limits as low as 0.1 to 0.01 parts per billion from 50 ml samples.

Table 1. Simultaneous Determination of Twenty-seven Elements by Spark-Source Mass Spectrometry in Typical Coal and Fly Ash Samples[a]

Element	Matrix Coal(1) (ppm)	 Fly Ash(1) (ppm)
Hg	0.08	<0.01
Be	1.2	8.0
Cd	0.19	0.70
As	0.30	22
V	12	50
Mn	30	400
Ni	2.7	50
Sb	0.14	4.5
Cr	4.5	110
Zn	10	260
Cu	25	200
Pb	3.9	60
Se	0.32	0.30
B	42	230
F	5.7	150
Li	--	42
Ag	0.22	0.50
Sn	0.83	60
Fe	1600	Major
Sr	100	2000
Na	5000	Major
K	410	7000
Ca	4000	Major
Si	Major	Major
Mg	4500	Major
U	1.9	30
Th	4.5	40

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[a] In addition to the above elements of interest, reference (1) lists values for 34-38 additional elements.

Table 2. Subject Index to References

I. Precision and/or Accuracy of SSMS Analysis
1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 13, 16, 17, 18, 23, 25, 26, 28, 32, 33, 34, 35, 36, 37, 38, 40, 41, 43, 51

II. Survey Analysis, Concentrations Estimated to Factor 3 to 10
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III. Analysis Using Synthetic Reference Standard
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IV. Analysis Using Certified Standard Reference Materials
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V. Analysis Using Isotope Dilution SSMS
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VI. Analysis of Solutions or Samples Dissolved for Analysis
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VII. Group I Samples - Coal, Oil, Organometallics and High Organic Content Samples
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VIII. Group II Samples - Fly Ash, Ores, Minerals, Slurry Streams, etc.
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X. Analysis Using Electronic Detection
1, 2, 5, 20, 22, 30, 31, 36, 37, 45, 49, 51, 52

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CHAPTER 4

X-RAY FLUORESCENCE AND ELECTRON MICROPROBE METHODS

Stanley D. Rasberry and Kurt F. J. Heinrich

1. X-RAY FLUORESCENCE

X-ray fluorescence analysis is noted for its applicability to a diversity of sample types and it has gained extensive industrial use for monitoring the composition of both raw materials and finished products. An introduction to the technique and descriptions of many applications are given in several books (references 1-6). The elements above atomic number 11 can be routinely determined in ores, minerals, fuels, bulk particulates, liquids, slurries, filtrates, powders, metals and other sample types. The applications of x-ray fluorescence analysis are being described in about 500 published papers per year. References 7-100 and 123-126, appended to this chapter, have been selected to represent recent applications.

The name x-ray fluorescence analysis is used to categorize several analytical techniques which have the same physical basis; inner-shell excitation of atoms induced via energy transfer from an incident flux of x-rays and the subsequent decay from excited state coupled with electron-atom recombination. The energy transfer, in both excitation and emission (decay) is dependent upon the atomic number (element) of the atom involved in the interaction. That is, an emitted fluorescent x-ray is characteristic in energy of the atom from which it is emitted. This gives the analyst a useful means of qualitatively identifying which elements are present in a specimen. As we shall see later, accurate quantitation depends in part on measuring the rate (intensity) at which x-rays of a given energy are emitted.

The apparatus necessary for x-ray fluorescence analysis includes a source of x-rays for excitation and a means of determining the rate of x-rays emitted from the specimen at discrete energies (the analyzer, detector and counting electronics). A variety of choices exists for each module of the instrument.

The excitation source may be an x-ray tube arranged to excite the specimen directly or through a filter so selected as to alter the excitation spectrum to more useful wavelengths. Another possible choice for excitation is the use of radioisotopes; here too, filters can be used. Outside the precise definition of fluorescent spectroscopy, excitation can also be effected by bombarding the specimen with electrons (10-100 keV), protons (1-200 MeV), or a variety of ions.

At the next stage in the apparatus, precise specimen positioning is required, and the excitation x-rays must be apertured so as to fall only on the specimen. The main options at this point consist of automated specimen changing or equipment for direct examination of continually flowing liquid, slurry or powder streams.

Various arrangements of collimation may be used either to aid reduction of background or improve energy resolution characteristics.

Separating the emitted x-rays into a spectrum of resolved energies is usually accomplished by one of three different means: diffraction, balanced filters, or "energy dispersive" analyzer. Diffraction of the x-ray beam by a crystal can be used to disperse the energies as an inverse function of beam-to-crystal angle. The dispersion characteristics are also a function of the lattice spacing of the crystal; but, this aspect is held constant with a given crystal selection. In the use of balanced filters, the filters are selected so that they transmit equal intensities at all energies except those between their absorption edges, and so that the energy of interest falls within this "band pass".

In both the diffractive and balanced filter modes, an x-ray detector must be employed to measure the presence and intensity of x-rays at a given energy. Scintillation detectors, gas-filled proportional detectors and gas-flow proportional detectors are used in different ranges of energies and count rates.

In the "energy dispersive" mode no physical separation of energies is used prior to the detector. Instead, energy separation is accomplished on the basis of pulse height analysis of the output signal of the detector. This is practicable because each x-ray energy produces an electronic pulse which is proportional in energy and thus susceptible to analysis. The detectors usually used in this mode are the Si(Li) solid state detectors because of their good energy resolution characteristics.

Each of the three means of energy analysis described has a large number of possible variations. This, together with the wide variety of excitation and detection possibilities, causes the number of permutations of instrument configurations to be large. One of the most generally effective arrangements for quantitative elemental analysis is shown in figure 1. This is the arrangement which has been used in most of the applications referred to in the bibliography. We have used it at NBS in the analysis of many different types of specimens. As an example, in figure 2 we show

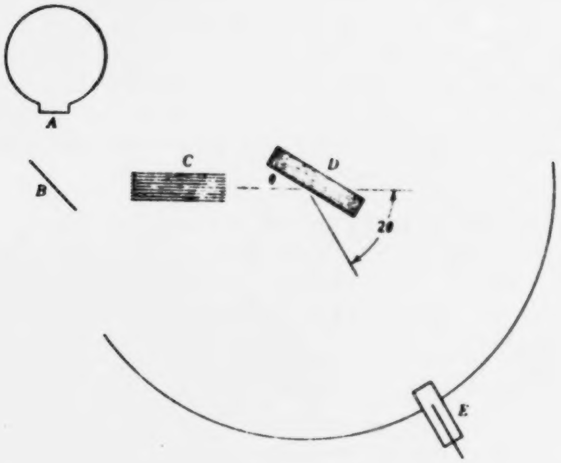

Figure 1. X-ray fluorescence analyzer. Flat crystal spectrometer geometry: (A) x-ray tube, (B) specimen, (C) collimator, (D) dispersing crystal, (E) detector, frequently preceded by a collimator (from reference 2).

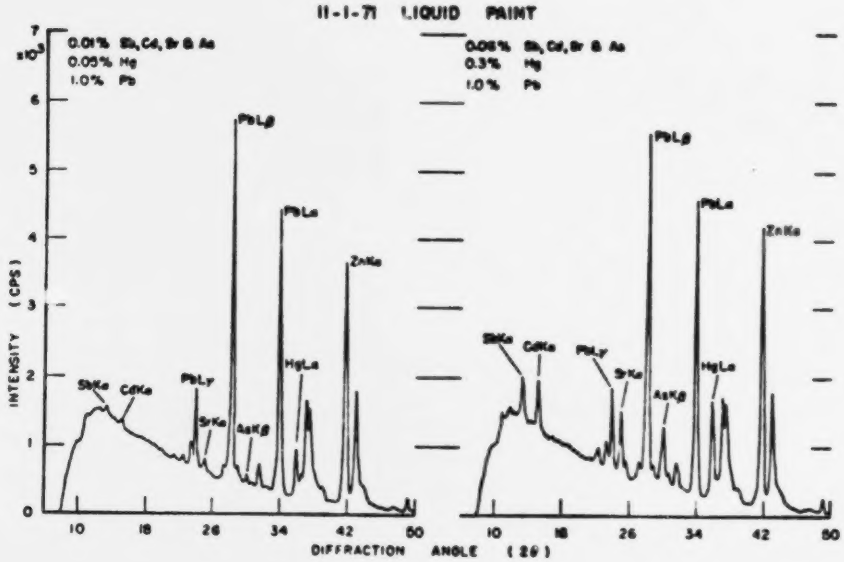

Figure 2. X-ray fluorescence spectra of liquid paints having two different levels of toxic metal content; obtained using a tungsten target tube operated at 50 kV, 50 mA, and LiF crystal and a scintillation detector.

the x-ray spectra of two samples of liquid paint. The spectrum on the right is for a paint with presence of antimony, cadmium, strontium, arsenic and mercury six-fold greater than in the paint represented on the left. At energies (x-ray lines) characteristic of these five elements, there is a nearly proportional increase in intensity -- demonstrating the feasibility of quantitative, as well as qualitative, analysis.

Quantitative determination of elements which do not vary over wide ranges of concentration (more than a few percent, by weight) in specimens of nearly constant composition is accomplished by use of standard reference materials or other known "type standards". It is important for the standards to be nearly the same in composition as the unknowns because of interelement effects which will be mentioned later. An example is given in figure 3 of a calibration curve prepared, at NBS, for the determination of lead in dry paint powder. The dry paint powder has been mixed with a common matrix to dilute the effects of differences in the remainder of the compositions.

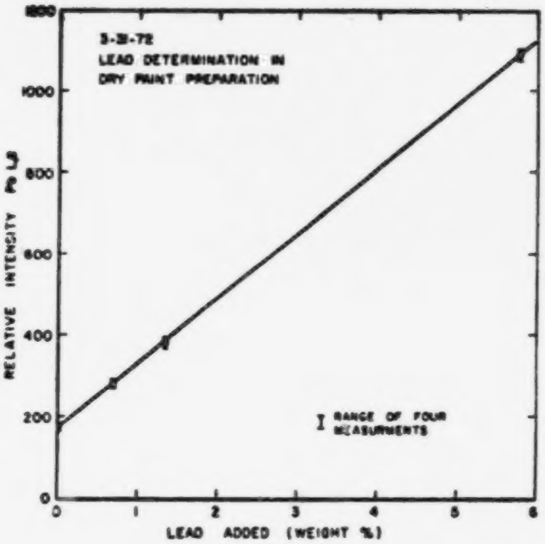

Figure 3. Calibration curve for determination of lead in dry paint powder, following preparation by dilution with a common matrix (ZnO); obtained using the same conditions as given in figure 2.

Usually, x-ray fluorescence analysis can be performed directly on a sample with little or no preliminary treatment; this results in low labor costs. For some types of samples, notably slurries, on-stream analysis is done for control purposes using automated equipment. The detection limit for direct analysis is usually 50-1000 ppm depending on the matrix and weight of sample available. For the more sensitive elements, or by using special preconcentration techniques, lower detection limits are achievable. Normally, one or two grams of material are used when this quantity is available. However, specimens as small as a few milligrams may be analyzed, possibly with reduced sensitivity, by using special methods. In industrial examples, the precision and accuracy available have permitted the economical analysis of such materials as steel, aluminum, glass and portland cement powder on an essentially real-time basis. The accuracy required in industry is typically ±1/2 percent to ±1 percent for the major elements, ±2 percent for the minor elements, and ±10 percent for the trace constituents.

X-ray fluorescence equipment is available for simultaneous determination of as many as ten or more elements, in the same sample, in a two-minute measurement period. Virtually every phase of the technique is susceptible to automation, from specimen preparation and insertion into the instrument through all measurement aspects, data collection, computation, interpretation and display. Especially when large volumes of analyses are done, automation is economically attractive owing to substantially decreasing labor costs. The instrument operators may be high school, vocational school or junior college-trained technicians; however, the supervision of the effort should be in the hands of a graduate chemist, chemical engineer or equivalent.

Interferences of two different types can occur in x-ray fluorescence. In the first (line interferences), an x-ray line of the analyte may be so near a line produced by another element that the two are not resolved by the spectrometer. Usually, this problem can be solved by selecting another x-ray line of the analyte to measure. The second kind of interference (matrix interelement effects) is caused when large differences in composition exist among the various standards and unknowns. The intensity of the x-ray line of the analyte is influenced not only by the analyte concentration, but also by the composition of the matrix (other elements). Correction procedures, either through chemical preparation or mathematical data manipulation are available to resolve this type of interference. Standard Reference Materials play a key role in the accurate calibration of x-ray fluorescence analysis.

Application to Matrices of Environmental Interest

1. Fly Ash and Incinerator Particulates. (references 7-19) Methods for the x-ray fluorescence analysis of fly ash and incinerator particulates were not actively researched until about five years ago. Since that time, extensive work has been done on the subject. As can be seen in the appended summary sheet, x-ray fluorescence methods are applicable for the determination of 24 of the 28 elements of principal interest. In routine direct analysis, the cost of determining one element should not exceed $1.00. Lower concentrations can be obtained by chemical pretreatment of the sample, with an attendant increase in cost (see references 18 and 19). The need for Standard Reference Materials seems **to be especially pressing for fly ash and incinerator particulate matrices.**

2. Coal. (references 20-23) L. T. Kiss (21) has made one of the best and most thorough studies of x-ray fluorescence analysis of coal presently available. Using a procedure of drying, fine-grinding and briquetting ten-gram samples of coal, x-ray measurement, and a special interelement correction procedure, Kiss was able to accurately determine from 0.02 percent to 3.90 percent of iron, titanium, calcium, potassium, chlorine, sulfur, silicon and aluminum in coal. Both synthetically prepared and chemically analyzed standards are used in calibration.

3. Oil. (references 24-37) X-ray fluorescence analysis of oils and gasolines is one of the oldest routine applications of the method -- dating back to the 1940's. Outstanding work has been done in this area by Birks, Brooks, Friedman and Roe (34), Dwiggins and Dunning (27-28), Hale and King (26) and Gunn (24-25). All elements above sodium can be determined in oil by x-ray fluorescence methods. Particular attention has been given to lead, bromine, molybdenum, nickel, iron, manganese, titanium, vanadium, zinc, calcium, and barium. Hale and King (26) report direct determination of nickel at the 0.1 ppm level, and Bergmann, Ehrhardt, Granatelli and Janik (30) report sub-ppm determinations using ion exchange preconcentration. The method is finding increased use (including work at NBS) in monitoring wear metals in engine and gearcase oils.

4. Ores, Minerals and Cement. (references 38-54) X-ray fluorescence analysis has found wide industrial acceptance in these areas over the past twenty years. This is especially true in the cement industry, where tens of thousands of determinations are performed each day using x-ray fluorescence spectrometers, many of which are highly automated. The work of Rose and Brown (38), Rose, Adler and

Flanagan (44) and Campbell and Thatcher (52) is especially important to the mining industry. Bean (48-49) and Andermann (50) are widely cited among investigators of x-ray fluorescence methods for the analysis of cement. When matrix variations are large, physically corrective techniques, such as dilution or mathematical treatment to correct the results are usually required. The need for standards is especially large in this area, and many have been produced by NBS, the most recent being seven new SRM's for portland cement to replace and supplement five others which were issued ten years ago.

5. Metals and Alloys. (references 55-79) Similar to the case of ores, minerals and cement, this area has been widely developed and used in industry over the past twenty years -- with significant improvement and further extension of application over the last five to ten years. The literature dealing with the analysis of metals and alloys by x-ray fluorescence is large (approximately 10,000 papers). The references given here are representative, but hardly do more than scratch the surface. The usual range for direct, accurate analysis is 0.01 percent to 95.0 percent for the elements above sodium in atomic weight. Research and development is active in this area, especially concentrating in: lower detection limits, more complete automation, more accurate standardization, and improved mathematical treatment. Several hundred Standard Reference Materials for metals and alloys have been issued by NBS. Alloy reference standards are also sold by U. S. Steel, Carpenter Technology, Brammer Standards, Alcoa and others.

6. Organometallics. (references 80-82, also see papers in section: Oil) The analysis of metallo-organic compounds is not a common subject in the x-ray fluorescence literature. However, metallo-organic compounds are used as additives in the preparation of synthetic oil standards. The literature pertinent to the x-ray fluorescence analysis of oil is described in the appropriate section. NBS has issued 24 metallo-organic compounds primarily to be used for the calibration of spectrochemical equipment used in the determination of wear metals in lubricating oil.

7. Slurry Streams, and Feeds and Sediments in Flotation Processes. (references 83-94) Smallbone (85 and 87) and Smallbone and Davidson (84 and 86) have been leaders in the design and construction of the special sample handling apparatus needed for "on-line" x-ray fluorescence applications. Calibration for these techniques is made difficult by the variability of water content in the moving material; corrections are required. Sampling is also an important aspect of the problem. Standardization is difficult, because to simulate the material under analysis requires flowing a

large volume of standard through the on-line sample handling apparatus. These problems cause undesirable losses in accuracy; further R and D appears to be needed in this area.

8. Slags and Glass. (references 95-100) An increasing amount of quality control analysis in the glass industry is done by x-ray fluorescence analysis. It is also a popular method for evaluating slags. Glasses are analyzed directly on solid material, with calibration by standards. NBS is supplying two Standard Reference Materials of solid glass and the ASTM is assisting in establishing several more on an inter-company basis. Until now, most companies have had only standards made in their own plants. The x-ray method is in a good state of development relative to glass analysis. Slags are usually treated with preparation techniques similar to those used for ores: crushing and briquetting, diluting and briquetting or diluting and fusion. The preparation of standards must follow the same process.

2. ELECTRON PROBE MICROANALYSIS

Electron probe microanalysis has been available, with commercially produced instruments, for about 15 years. During that time many industrial applications have been described in the literature. A survey of these is given in references 101-122.

Electron probe microanalysis is the sum of procedures using a focused electron beam (of energy between 1 and 50 keV) to obtain, from the zone of beam impact upon a specimen, information concerning its properties. This is achieved in an instrument similar in some aspects to the electron microscope. Electrons emitted from a heated tungsten wire are focused into a beam of a diameter of less than 0.5 µm. This beam is directed toward the specimen. The interaction of the specimen with the impinging electron beam results in the emission of x-ray lines from the microscopic region of the specimen which has been excited by the electrons. The characteristic x-ray spectra emitted by the specimen reveal its elemental composition.

The emitted x-ray lines can be observed, and their intensities measured, by means of curved-crystal spectrometers. The instrument at NBS has three such spectrometers, so that three elements can be measured simultaneously. The wavelength range is from 1 to 100 Å; this permits the observation and analysis of all elements of atomic number above 5, and with high sensitivity for the elements of atomic number above 10. Another device installed in the NBS electron probe is the energy dispersive solid state detector. This device permits the simultaneous detection of all elements of atomic number above 11, and thus provides for a rapid means for qualitative and semiquantitative analysis, which is particularly useful in the analysis of small particles.

Other phenomena (emission of backscattered and secondary electrons, cathodoluminescence, etc.) also produce useful information. The analyzed region on the specimen which is excited by the electron beam is usually about 2 x 2 x 2 µm. Since Cosslett and Duncumb (128) introduced the scanning beam technique in electron probe microanalysis, the instrument has become a microscope as well as a spectrometer. The interactions between scanning electron microscopy and x-ray spectrometry account for the great versatility of this instrument. It has found wide industrial application both for the analysis of free-standing microparticulates and for microscopic features on the surfaces of bulk materials.

The forte of the electron probe is microanalysis (small size) as opposed to trace analysis (low concentration); however, detection limits between 100 and 1000 ppm are available for most elements. Accuracies of ± 5 percent, or better, are routinely available and careful, quantitative work can produce accuracies of ±2 percent. The precision of measurement, for elements above 1 percent in concentration, is generally ±1 percent or better.

Sample preparation depends on the nature of the specimen. If the specimen is larger than one inch in diameter, a sample must be cut so that it will be small enough (one-inch diameter) to load in the instrument. Discrete micro-particulates can be isolated, mounted and restrained. Quantitative analysis of metals requires a flat polish, equivalent to that obtained with 1/4-µm diamond polishing compound. Nonconductive specimens are given a sub-µm coating of a conductor (usually carbon) in a vacuum evaporator so that static charging will not occur when the samples are subjected to the electron beam. In some cases, especially for qualitative work, no sample preparation is required.

The cost for purchase of an electron probe microanalyzer, auxiliary equipment and sample preparation facilities is about $150K to $200K. Operational cost for an electron probe laboratory, including labor costs, may be expected to range between $250 and $500 per day. A single element determination on a single point on a sample requires about one-half hour; economies may result when several elements are determined at several points on the same sample. As with x-ray fluorescence, the instrument operators may be non-degree technicians, but supervision should be in the hands of a graduate chemist, or equivalent.

The conditions for electron probe microanalysis and the results to be expected are quite similar for all sample types which can be analyzed, therefore, a single guideline for application is appended. Usually the electron probe analysis is considered applicable to particulates isolated from fly ash or from incinerators; or even, particulates from slurry streams or in sediments from flotation processes. In addition, it is applicable to analyses in coal, ores, minerals, cement, metals, alloys, slags and glasses. To the best of our knowledge it has not been applied to analysis of oil or organometallics. It would be feasible, however, to perform such analyses on solid particulate wear residues in lubricating oils.

3. ION PROBE MICROANALYZER

The usefulness of the electron probe microanalyzer in the determination of trace levels is limited by the background which is inherent to primary x-ray spectra. This background is principally produced by the continuous (bremsstrahlung) spectrum. As to the elements which can be investigated, the electron probe is inefficient or useless for the investigation of elements of atomic number below ten.

The ion probe microanalyzer offers a promising alternative to the electron probe. In this instrument, the probe-forming agent is an ion beam, which can be of either negative or positive charge. Ions of several elements can be used, although oxygen is presently the preferred species. The beam can be focused into a focal spot in the order of one or a few micrometers, and it can be scanned in line- or raster form, in the same manner as the electron beam in a scanning electron microscope. The secondary ions formed in the sputtering of the specimen are collected in a mass spectrograph, and the spectrum thus obtained is used to identify the elements present in the specimen.

Secondary mass spectra can be obtained from all elements of the periodic table, with particularly high sensitivity for the atomic numbers below ten which cannot be efficiently handled with the electron probe. Further advantages of the ion probe are: the shallow sampling (100 angstroms or less), the possibility of measuring isotope ratios, and the possibility of producing depth profiles, due to the etching action of the primary beam which removes successive layers of the specimen material. The method is, however, still in an experimental stage, particularly with reference to its potentials for quantitation. Due to the complexity of the underlying physical process, the accuracy of ion probe analysis is probably inherently lower than that of electron probe analysis, except for isotope ratio measurements, which can be performed to one percent accuracy or better.

The technique is applicable to a large range of specimens. The analysis of individual microscopic particles of air particulates has been demonstrated in practice, and it thus appears that this instrument may have an important role in the study of environmental and pollution problems (129).

Table 1. Analysis of Fly Ash and Incinerator Particulates by X-Ray Fluorescence

Element(a)	Expected Conc'n. (ppm)	Accuracy (%)	Time to Prepare Sample (min)	Sample Size (g)	Detection(b) Limit (ppm)	Cost(c) Per Analysis ($)	References
Hg	(d)	5-25	5	1-10	500	1-5	See 7-19, especially:
Cd	10-100	15	"	"	100	"	
As	100	15	"	"	100	"	
V	500	5	"	"	50	"	
Mn	1000	5	"	"	50	"	
Ni	500	5	"	"	10	"	
Sb	10	25	"	"	100	"	
Cr	100	15	"	"	50	"	
Zn	5000	5	"	"	50	"	14
Cu	1000	5	"	"	50	"	
Pb	5000	5	"	"	200	"	12,16,17
Se	(d)		"	"	100	"	
Ag	(d)		"	"	100	"	
Sn	100	15	"	"	100	"	
Fe	1-10%	5	"	"	50	"	
Sr					200		
Na	(e)	15	"	"	1-2%	"	
K	(e)	5	"	"	200	"	
Ca	(e)	5	"	"	100	"	
Si	(e)	5	"	"	200	"	
Mg	(e)	5	"	"	1000	"	
U	(d)		"	"	500	"	
Th	(d)		"	"	500	"	
S	(e)	5	"	"	200	"	7,19

(a) Determination of Be, B, F, Li not feasible by XRF.
(b) See text for equipment required, manpower skills, and interferences expected.
(c) Ten elements may be determined for $10-50 total, in routine analysis.
(d) Expected levels not known. May be 1-10 ppm or less.
(e) Major constituents.

Table 2. Analysis of Coal by X-Ray Fluorescence

Element[(a)]	Expected Conc'n. (ppm)	Accuracy (%)	Time to Prepare Sample (min)	Sample Size (g)	Detection[(b)] Limit (ppm)	Cost[(c)] Per Analysis ($)	References
							See 20-23,
Hg			30	10	500	5-10	especially:
Cd			"	"	100		
As			"	"	100		
V			"	"	50		
Mn			"	"	50		
Ni			"	"	10		
Sb			"	"	100		
Cr			"	"	50		
Zn			"	"	50		
Cu			"	"	50		
Pb			"	"	200		
Se			"	"	100		
Ag			"	"	100		
Sn			"	"	100		
Fe	0.5-10%	5	"	"	50		21,23
Sr			"	"	200		
Na	0.01-3%	25	"	"	1-2%		23
K	0.01-0.5%	25	"	"	200		21,23
Ca	0.1-10%	5	"	"	100		21,23
Si	0.5-10%	5	"	"	200		21,23
Mg	0.1-1%	5	"	"	1000		23
U					500		
Th					500		
S	0.3-6%	5	"	"	200		20,23
Al	0.5-10%	5	"	"	200		21,23
Ti	2000	5	"	"	10		21,23
Cl	0.04-0.20	15	"	"	200		21

(a) Determination of Be, B, F, Li not feasible by XRF.
(b) See text for equipment required, manpower skills, and interferences expected.
(c) Ten elements may be determined for $50-100 total, in routine analysis.

Table 3. Analysis of Oil and Organometallics by X-Ray Fluorescence

Element[(a)]	Expected Conc'n. (ppm)	Accuracy (%)	Time to Prepare Sample (min)	Sample Size (g)	Detection[(b)] Limit (ppm)	Cost[(c)] Per Analysis ($)	References
Hg			5	10	500	4-10	See 24-37,80-82, especially:
Cd			"	"	100	"	
As			"	"	100	"	
V	100-500	5	"	"	2	"	28
Mn	5%	1	"	"	50	"	35
Ni	0.1-100	5	"	"	0.1	"	24,27
Sb			"	"	100	"	
Cr			"	"	50	"	
Zn	100-500	15	"	"	50	"	31
Cu			"	"	50	"	
Pb	500	15	"	"	200	"	31
Se			"	"	100	"	
Ag			"	"	100	"	
Sn			"	"	100	"	
Fe	1-100	15	"	"	1	"	28
Sr			"	"	200	"	
Na			"	"	1-2%	"	
K			"	"	200	"	
Ca	0.1-1%	5	"	"	100	"	31
Si			"	"	200	"	
Mg			"	"	1000	"	
U			"	"	500	"	
Th			"	"	500	"	
S	0.1-5%	15	"	"	100	"	28
Al			"	"	200	"	
Ti			"	"	10	"	

(a) Determination of Be, B, F, Li not feasible by XRF.
(b) See text for equipment required, manpower skills, and interferences expected.
(c) Five elements may be determined for $20-50 total, in routine analysis.

Table 4. Analysis of Ores, Minerals and Cements by X-Ray Fluorescence

Element$^{(a)}$	Expected$^{(b)}$ Conc'n. (ppm)	Accuracy$^{(c)}$ (%)	Time to Prepare Sample (min)	Sample Size (g)	Detection$^{(d)}$ Limit (ppm)	Cost$^{(e)}$ Per Analysis ($)	References
Hg		5	5-30	2-10	500	1-10	See 38-54, especially
Cd		"	"	"	100	"	
As		"	"	"	100	"	
V		"	"	"	50	"	
Mn		"	"	"	50	"	
Ni		"	"	"	10	"	
Sb		"	"	"	100	"	
Cr		"	"	"	50	"	
Zn		"	"	"	50	"	
Cu		"	"	"	50	"	
Pb		"	"	"	200	"	
Se		"	"	"	100	"	
Ag		"	"	"	100	"	
Sn		"	"	"	100	"	
Fe		"	"	"	50	"	
Sr		"	"	"	200	"	
Na		"	"	"	1-2%	"	
K		"	"	"	200	"	
Ca		"	"	"	100	"	
Si		"	"	"	200	"	
Mg		"	"	"	1000	"	
U		"	"	"	500	"	
Th		"	"	"	500	"	
S		"	"	"	200	"	

(a) Determination of Be, B, F, Li not feasible with XRF.
(b) Concentrations depend on samples and stages of processing.
(c) Accuracy generally ±5 percent for main elements.
(d) See text for equipment required, manpower skills, and interferences expected.
(e) Cost in direct, automated systems less than $1 per element; in manual systems with preparation, $10 per element.

Table 5. Analysis of Metals and Alloys by X-Ray Fluorescence

Element[a]	Expected[b] Conc'n. (ppm)	Accuracy[c] (%)	Time to Prepare Sample (min)	Sample Size	Detection[d] Limit (ppm)	Cost[e] Per Analysis ($)	References
Hg		2-5	1-10	Usually Bulk	500	1	See 55-79
Cd		"	"		100	"	
As		"	"		100	"	
V		"	"		50	"	
Mn		"	"		50	"	
Ni		"	"		10	"	
Sb		"	"		100	"	
Cr		"	"		50	"	
Zn		"	"		50	"	
Cu		"	"		50	"	
Pb		"	"		200	"	
Se		"	"		100	"	
Ag		"	"		100	"	
Sn		"	"		100	"	
Fe		"	"		50	"	
Sr		"	"		200	"	
Na		"	"		1-2%	"	
K		"	"		200	"	
Ca		"	"		100	"	
Si		"	"		200	"	
Mg		"	"		1000	"	
U		"	"		500	"	
Th		"	"		500	"	
S		"	"		200	"	

(a) Determination of Be, B, F, and Li not feasible with XRF.
(b) Concentrations depend on metal samples.
(c) Accuracy generally ±2-5 percent for main and minor elements.
(d) See text for equipment required, manpower skills, and interferences expected.
(e) In industrial applications, usually less than $1 per element.

Table 6. Analysis of Slurry Streams, Feeds and Sediments by X-Ray Fluorescence

Element[(a)]	Expected[(b)] Conc'n. (ppm)	Accuracy[(c)] (%)	Time to Prepare Sample (min)	Sample Size (g)	Detection[(d)] Limit (ppm)	Cost[(e)] Per Analysis ($)	References
Hg		15	0-30	1-10	500	1	See 83-94
Cd		"	"	"	100	"	
As		"	"	"	100	"	
V		"	"	"	50	"	
Mn		"	"	"	50	"	
Ni		"	"	"	10	"	
Sb		"	"	"	100	"	
Cr		"	"	"	50	"	
Zn		"	"	"	50	"	
Cu		"	"	"	50	"	
Pb		"	"	"	200	"	
Se		"	"	"	100	"	
Ag		"	"	"	100	"	
Sn		"	"	"	100	"	
Fe		"	"	"	50	"	
Sr		"	"	"	200	"	
Na		"	"	"	1-2%	"	
K		"	"	"	200	"	
Ca		"	"	"	100	"	
Si		"	"	"	200	"	
Mg		"	"	"	1000	"	
U		"	"	"	500	"	
Th		"	"	"	500	"	
S		"	"	"	200	"	

(a) Determination of Be, B, F, Li not feasible with XRF.
(b) Concentrations depend on materials being analyzed.
(c) Accuracies frequently not better than ±15 percent because of calibration difficulties.
(d) See text for equipment required, manpower skills, and interferences expected.
(e) In industrial applications, usually less than $1 per element.

Table 7. Analysis of Slags and Glasses by X-Ray Fluorescence

Element(a)	Expected(b) Conc'n. (ppm)	Accuracy(b) (%)	Time to Prepare Sample (min)	Sample Size (g)	Detection(c) Limit (ppm)	Cost(d) Per Analysis ($)	References
Hg			5-30	2-10	500	1-10	See 95-100
Cd	(e)		"	"	100	"	
As			"	"	100	"	
V	(e)		"	"	50	"	
Mn	(e)		"	"	50	"	
Ni	(e)		"	"	10	"	
Sb	(e)		"	"	100	"	
Cr	(e)		"	"	50	"	
Zn	(e)		"	"	50	"	
Cu	(e)		"	"	50	"	
Pb	0-5%	5	"	"	200	"	
Se	(e)		"	"	100	"	
Ag			"	"	100	"	
Sn	(e)		"	"	100	"	
Fe	0-3%(f)	5	"	"	50	"	
Sr	(e)		"	"	200	"	
Na	0-20%	15	"	"	1-2%	"	
K	0-5%	15	"	"	200	"	
Ca	(g)	5	"	"	100	"	
Si	(g)	1	"	"	200	"	
Mg	0.01-5%	5	"	"	1000	"	
U			"	"	500	"	
Th			"	"	500	"	
S			"	"	200	"	

(a) Determination of Be, B, F, Li not feasible with XRF.
(b) Elemental concn. and accuracy of determination are sample-dependent.
(c) See text for equipment required, manpower skills, and interferences expected.
(d) Direct, automated systems less than $1 per element; manual systems with preparation, **$10 per element.**
(e) Possibly present in both slags and glasses.
(f) Higher in slags.
(g) Major constituent in slags and glasses.

Table 8. Analysis of Particulates by the Electron Probe Microanalyzer

Element	Expected[(a)] Conc'n. (ppm)	Accuracy[(a)] (%)	Detection[(b)] Limit (ppm)	Cost[(c)] Per Analysis ($)	References
Hg			0.1%	5-50	See 101-122
Be				"	
Cd			200	"	
As			200	"	
V			100	"	
Mn			100	"	
Ni			100	"	
Sb			200	"	
Cr			100	"	
Zn			100	"	
Cu			100	"	
Pb			200	"	
Se			200	"	
B				"	
F				"	
Li				"	
Ag			200	"	
Sn			200	"	
Fe			100	"	
Sr			200	"	
Na			1%	"	
K			200	"	
Ca			100	"	
Si			100	"	
Mg			500	"	
U			500	"	
Th			500	"	

(a) Elemental concentration and accuracy of determination are sample-dependent.
(b) See text for equipment required, time to prepare sample, sample size, manpower skills, and interferences.
(c) Automated systems about \$5 per element, manual systems with preparation about \$50 per element.

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CHAPTER 5

ATOMIC ABSORPTION SPECTROMETRY

Theodore C. Rains

1. INTRODUCTION

Atomic absorption spectrometry (AAS) has been demonstrated to be a sensitive and selective technique for inorganic analysis (1-4). This technique is presently being used to determine the major, minor and trace elements in a wide variety of materials such as water, petroleum products, metals, ores, air particulates and biomedical materials. In atomic absorption methods of chemical analysis, a portion of the sample is converted into an atomic vapor, and the absorbance of light by this vapor is measured at a specific wavelength which is characteristic of the analyte. The unknown concentration is determined by comparison with absorbance measurements on standards of known composition.

The advantages of AAS may be summarized as (1) the large number of elements which can be determined with one instrument, (2) the low limits of detection, (3) the relative freedom from interferences, (4) the speed of analysis with no elaborate separations required, and (5) the absence of need for highly trained technical personnel for most types of AAS analysis.

2. INSTRUMENTATION AND TECHNIQUE

A wide range of AAS instruments for making accurate and precise measurements is commercially available. The basic components of an AAS instrument consist of a primary source of radiation, a means of producing atomic vapor, a wavelength isolator, radiation detector and readout system.

In general, hollow-cathode lamps are used as the primary source of radiation; they are available commercially for all elements which can be determined by AAS. As a rule they meet the basic requirements and are readily applicable to all AAS instruments.

The conventional means of producing atomic vapor of the analyte is to nebulize the sample solution into a flame. This is a wasteful and inefficient process but it is simple and convenient, and hence continues to be used. In recent years, nonflame sources have been used to produce atomic vapor (5). Examples of such devices include plasma torches, stabilized arcs and heated graphite furnaces. Of these three sources the heated graphite furnace has advantages over flame methods in greater sensitivity, lower detection limits, and the ability to accommodate very small samples (0.5 to 50 µl). The main factors in the production of atomic vapor are (a) efficiency of atomization, (b) length of flame or nonflame cell, (c) oxidant-fuel used to produce atomic vapor, and (d) position within atomic vapor in which absorption measurements are made.

Requirements for the wavelength selector may vary considerably from element to element. Basically, it is essential to be able to separate the one required spectral line from all others, and to keep any background intensity to a minimum. The means by which this is achieved may vary from a simple filter, in the case of sodium, to a high resolution monochromator with a band pass of 1 Å for the determination of nickel, iron and cobalt. If background radiation is emitted by the primary source of radiation, a narrow band pass in the selector will minimize its effect. There are some special instances where a narrow band pass is required to avoid interferences due to the selection of more than one absorption line.

To detect the radiation, a multiplier phototube with its associated power supply and measuring system are essential for high sensitivity and precision. Because the detection system is affected directly by the stability of the measuring circuit, the multiplier phototube, power supply, amplifier, and readout system must be sensitive and stable. At present, many types of multiplier phototubes and associated electronics are available commercially.

Seventy elements have been determined by AAS with detection limits in an aqueous media of 10 to 10^{-4} µg/ml. With non-flame methods such as the carbon rod atomizer, the detection limits for 33 of these elements have been extended to an absolute value of 10^{-11} to 10^{-14} grams, and this list of elements is growing almost daily.

A. Interferences

Interferences do occur in varying degrees for all elements determined by AAS. Interferences can be classified as physical or chemical (10). Physical interferences are effects which are caused by a physical property of the sample solution, or which alter one of the physical processes involved in the atomization process. Of all the physical interferences, light scattering by particles in the atomization process usually is the most troublesome. Techniques have been developed using background correctors but the analyst must be alert to the possibility of light scatter, especially for those elements emitting in the ultraviolet region of the spectrum, and apply the proper correcting technique.

Chemical interferences are classified as condensed phase, ionization, and mutual. Condensed phase interference occurs when a concomitant (element, radical, or solute present in solution) inhibits the dissociation or excitation of the analyte, thereby suppressing the signal. Ionization interference occurs when the analyte is ionized in the flame causing a reduction in signal strength. Mutual or interelement interference is not well understood but it has been observed, particularly in the nitrous oxide - acetylene flame, that the presence of a particular element may enhance or suppress the absorption due to an analyte.

To eliminate or control chemical interferences in AAS it is essential that the various instrumental parameters be optimized. These include type of burner, oxidant-fuel ratio, flame temperature, flame region, and sample. The flame or atomization temperature plays a major role in determining the extent of chemical interference. With the high temperature nitrous oxide - acetylene flame the chemical interference of aluminum, titanium, silicon, sulfate, or phosphate on the alkaline-earth metals is removed. However, this high-temperature flame usually introduces another type of interference which is caused by ionization of the analyte, but this can be controlled by the addition of a cation having a similar or lower ionization potential than that of the analyte.

Another way to eliminate condensed phase type of interference is by the addition of releasing or protective chelating agents. Releasing or protective chelating agents are defined as substances which, when added in sufficient quantity in the presence of an interferent, will restore the absorption of the analyte to its original value.

In some extreme cases liquid-liquid extraction is used to remove the interferent; this has an added effect of increasing the sensitivity of the analysis by preconcentrating the analyte.

3. SAMPLE REQUIREMENTS

The kinds of samples suitable for analysis by atomic absorption spectrometry cover a wide range. The analyte may be present in only trace quantities or it may be a major constituent. The type and quantity of sample being analyzed usually affect the selection of a sampling method and sample preparation. Trace analysis frequently requires special sampling and preparation techniques. Some factors which must be considered are (a) the sampling process, (b) procedures for obtaining samples in solution, and (c) methods of separation or preconcentration, if required. The nature of the sample matrix (e.g. coal, fly ash, ores, minerals, metals, etc.) governs the choice of sampling, dissolution, and preconcentration steps.

A. Sampling

A particular sampling approach which the analyst should follow is dictated by the concentration of the analyte and the specific purpose for the analysis. The sampling procedure or the lack of sample homogeneity have been known to introduce errors much greater than those associated with the chemical determinations. Calder (65) has shown that in the analysis of potassium in herbage, the variance due to sampling was ten times greater than the variance for the flame determinations.

B. Sample Preparation

The procedures for sample dissolution and subsequent treatment depend upon the sample matrices being analyzed; naturally, one method of sample treatment cannot be expected to work well for all matrices, and it is necessary to choose the best approach for any particular sample. A review of various techniques for the preparation of samples for AAS analysis has been made, which includes biochemical, agricultural, metallurgical, mining, geochemical, industrial, and other types of samples (5-7).

At the present state-of-the-art, solutions are normally required for atomic absorption spectrometry. A new technique using a carbon rod or furnace is currently being developed which holds promise that solid samples (e.g. fly ash, air particulates, etc.) may soon be analyzed directly; but the overwhelming majority of present-day AAS determinations is made on solutions.

Sample Dissolution

Samples with a high content of organic material respond well to dry ashing (heating for 2-4 hours at 500°C) with subsequent dissolution of the residue in a mineral acid. If wet ashing is preferred, the sample may be heated with a mixture of nitric and perchloric acids, though other combinations of acids with sulfuric acid are preferred for some matrices. Most metals and alloys are soluble in hydrochloric and nitric acids. If silicates and the more refractory elements are present, the addition of hydrofluoric acid is essential. To dissolve the more refractory ores and minerals, the sample may be decomposed in a specially designed Teflon vessel with hydrofluoric acid and a small quantity of aqua regia. The time required for decomposition is 30-40 min at a temperature of 110°C.

It is important that the acids used for dissolving the samples be of such purity that they do not contribute trace elements of their own to the analytical results.

Separation or Preconcentration

Separation or preconcentration or both are frequently required as a part of AAS determination of trace elements. Separation methods, as distinct from preconcentration steps, are normally utilized to separate the analyte from the matrix or from other interfering species. Preconcentration steps are performed when the sensitivity or detection limits of the method are insufficient for the analysis. Due to the high specificity of AAS analyses, it is possible in most instances to perform a general, nonspecific separation and preconcentration step for one or several elements. The methods of separation and preconcentration are liquid-liquid extraction, ion exchange and coprecipitation. Of these three methods, liquid-liquid extraction is preferred and used extensively in atomic absorption spectrometry. Chelating agents most frequently used include 8-quinolinol (oxine), dithizone (diphenylthiocarbazone), cupferron, and several dithiocarbamate derivatives, particularly diethylammonium diethyldithiocarbamate and ammonium pyrrolidine dithiocarbamate (7). The chelates formed are extracted into a water - immiscible, nonaqueous solvent such as methyl isobutyl ketone (MIBK). After removal of the aqueous phase, the metal-bearing organic phase is introduced into the flame and the absorption measured. This technique not only separates the analyte from the matrix, but also yields an increase in sensitivity due to the effect of the organic solvent on the flame.

4. APPLICATION TO MATERIALS OF ENVIRONMENTAL INTEREST

Atomic absorption spectrometry has been compared with other spectrochemical methods (8) and with other techniques of chemical analysis (9) for a variety of materials. In many laboratories AAS has supplanted wet chemical methods due to its specificity, low limits of detection, capability of determining many elements in one sample solution, freedom from elapsed-time requirements of those methods in which reactions must go to completion, and provision for data output in digital-concentration form.

In the past five years papers have been published describing AAS techniques for diverse environmentally impacting materials which include agricultural - fertilizer, plants, and soils; clinical - air, blood, tissue and hair, urine and bone; industrial - cement, chemicals, coal, gasoline and liquid fuels, lubricating oils, pharmaceuticals, and polymers; nutritional - beverages, fats and foodstuffs;

metallurgical - iron and steel, ferrous and non-ferrous alloys and refractory materials; mining and geochemical - minerals, ores, silicates and water samples. It appears that AAS has been used to analyze almost every known type of material.

5. RESULTS AND CONCLUSIONS

A. Tabulated Information

Tables 1-6 summarize the literature described in references 1-65. Detection limits, required sample sizes, and analytical costs are collected for the elements of interest at expected concentrations in the range 1, 10, and 100 ppm. At these levels the expected accuracy of AAS analyses is 25 percent, 15 percent, and 5 percent respectively. This contrasts with the instrumental precision of AAS analysis of 1-2 percent and analytical accuracy of better than 2 percent at macro concentration levels. The attainment of these expected levels of accuracy in the analyses depends on the continued use of reliable standards.

Stock solutions of standards are prepared from high purity metals which are available as NBS Standard Reference Materials (SRM's). Procedures for the preparation of 77 standard solutions are described by Dean and Rains (5). The quality of the standards used during the analytical measurements is of great importance in trace element determinations.

Column 10 in tables 1-6 is an element index to the references, and provides entry to additional information on individual elements in specific matrices. No literature was available on the direct determination of fluorine and thorium by atomic absorption spectrometry.

B. Costs

No great operator skill or experience are needed to operate AAS instruments, and less operational dexterity is required with flame methods than with most other types of spectroscopic sources. However, training in the observation of possible causes of error is essential for trace element determinations. Hazards to the operator are few, but proper safety precautions must be learned and practiced, especially when using nitrous oxide - acetylene flames.

Atomic absorption spectrometers are relatively inexpensive, with a price range of $3,500 to $12,000. The estimated analytical costs may be expected to decrease from the values listed in the tables, as the number of elements to be determined in the same solution is increased. Atomic absorption spectrometry appears to be capable of providing an analytical capability which can meet the financial requirements of most industrial and municipal laboratories.

C. Conclusions

Atomic absorption spectrometry is a versatile analytical tool which can be used to determine 25 of 27 elements of interest present in macro or trace concentrations as constituents in environmentally significant matrices. Its high specificity, moderate instrument and labor requirements, and simple operating procedure make it eminently suited for routine trace element determinations at a reasonable cost.

Table 1. Analysis of Metals and Alloys by Atomic Absorption Spectrometry Flame Method

Element	Expected Conc'n. (ppm)	Accuracy (%)	Eqpt. Req'd. (a)	Time to Prepare Sample (hr)	Sample Size (g)	Detection Limit (μg/g)	Cost(f) Per Analysis ($)	Comments	References
Hg	1,10,100	25,15,5	A	2-4	1-5	1	50-100		38,53
Be	"	"	B	2-4	0.1-1	0.3	40-60	(b)	6,7,14
Cd	"	"	C	2-4	.01-.1	0.1	20-40	(b)	6,7,14,62
As	"	"	D	2-4	0.1-1	0.2	20-40	(b,e)	7,14,44
V	"	"	B	2	0.1-1	0.2	20-40	(b)	7,14,22,19
Mn	"	"	C	2-4	0.1-1	0.1	40-60		6,7,14,19
Ni	"	"	C	2	0.1-1	0.1	20-40	(b)	6,7,14,19
Sb	"	"	C	2-4	0.1-1	0.1	40-60	(b)	14,22,61
Cr	"	"	C	2	0.1-1	0.5	20-40	(b)	6,7,14,19
Zn	"	"	C	2	0.1-1	0.1	20-40	(b)	19,22,62
Cu	"	"	C	2	0.1-1	0.2	20-40	(b)	7,19,22,41
Pb	"	"	C	2	0.1-1	0.1	20-40	(b)	7,22,41,61
Se	"	"	C	2-4	0.1-1	0.2	40-60	(b)	7,22,54
B	10,100	15,5	B	2-4	1-5	10	50-100		7
F	No information.								
Li	1,10,100	25,15,5	C	2	0.1-1	0.01	20-40		6,7,19,22
Ag	"	"	C	2	0.1-1	0.1	20-40	(b)	7,19,22,41
Sn	"	"	C	2-4	0.1-1	0.1	40-60	(b)	43,61
Fe	"	"	C	2	0.1-1	0.1	20-40	(b)	6,7,19,22
Sr	"	"	C	2	0.1-1	0.1	20-40	(c)	7,22,56
Na	"	"	C	2	0.01-.1	0.01	20-40		6,7,22,56
K	"	"	C	2	0.01-.1	0.01	20-40		6,7,22,56
Ca	"	"	B	2	0.1-1	0.1	20-40	(c,d)	7,19,22
Si	10,100	15,5	B	4-6	1-5	1	40-60		7,22
Mg	1,10,100	25,15,5	C	2	0.1-1	0.1	20-40	(d)	6,7,19,22
U	10,100	15,5	B	2-4	1-5	10	50-100		7
Th	No information.								

(a) AAS, plus oxidants and fuels: A=$Ar+H_2$; B=$N_2O+C_2H_2$; C=$Air+C_2H_2$; D=$Air+H_2$.
(b) Separation and preconcentration required for 1 ppm.
(c) Releasing agent required ($LaCl_3$).
(d) Ionization suppressor required.
(e) Molecular scatter.
(f) Costs include nontechnical personnel skilled in AAS analyses.

Table 2. Analysis of Fly Ash, Ores and Minerals by Atomic Absorption Spectrometry Flame Methods

Element	Expected Conc'n. (ppm)	Accuracy (%)	Eqpt. Req'd. (a)	Time to Prepare Sample (hr)	Sample Size (g)	Detection Limit (μg/g)	Cost(e) Per Analysis ($)	Comments	References
Hg	1,10,100	25,15,5	A	2-4	1-5	1	50-100		6,53
Be	"	"	B	2-4	0.1-1	0.5	50-100		19,41,49
Cd	"	"	C	2-4	0.01-1	0.1	40-60	(b)	22,41,50,51
As	"	"	A	2-4	0.1-1	0.2	40-60	(b)	44,47,51
V	"	"	B	2-4	0.1-1	0.6	40-60		22,51
Mn	"	"	C	2-4	0.1-1	0.1	40-60		22,51
Ni	"	"	C	2-4	0.1-1	0.1	40-60	(b)	25,27,41
Sb	"	"	A	2-4	0.1-1	0.1	40-60	(b)	6,7,22
Cr	"	"	B	2-4	0.1-1	0.5	40-60		6,7,19,51
Zn	"	"	C	2-4	0.1-1	0.1	40-60	(b)	22,23,45,50,59
Cu	"	"	C	2-4	0.1-1	0.2	40-60	(b)	22,41,51
Pb	"	"	C	2-4	0.1-1	0.2	40-60	(b)	22,23,41
Se	"	"	A	2-4	0.1-1	0.2	40-60	(b)	22,47,54
B	10,100	15,5	B	2-6	1-5	10	50-100		48
F	No information.								
Li	1,10,100	25,15,5	C	2-4	0.01-1	.01	40-60		7,22,56
Ag	"	"	C	2-4	0.1-1	0.2	40-60	(b)	22,23,41
Sn	"	"	A	2-4	1-5	1	50-100	(b)	22,50
Fe	"	"	C	2-4	0.1-1	0.1	40-60		7,22,45,56
Sr	"	"	C	2-4	0.1-1	0.1	40-60	(c)	22,45
Na	1,10,100	25,15,5	C	2-4	0.01-.1	.01	40-60		7,27
K	"	"	C	2-4	.01-.1	.01	40-60		27,46
Ca	"	"	B	2-4	0.1-1	.1	40-60	(d)	6,27,46,51
Si	10,100	15,5	B	2-6	1-5	1	50-100		7,22,46
Mg	1,10,100	25,15,5	C	2-4	0.1-1	.1	40-60	(c)	7,27,45,46
U	10,100	15,5	B	2-4	1-5	10	40-60		7
Th	No information.								

(a) AAS, plus oxidants and fuels: A=$Ar+H_2$; B=$N_2O+C_2H_2$; C=Air-C_2H_2.
(b) Separation and preconcentration required for 1 ppm.
(c) Releasing agent required ($LaCl_3$).
(d) Ionization suppressor required.
(e) Costs include nontechnical personnel skilled in AAS analyses.

Table 3. Analysis of Fly Ash, Ores, Minerals, Metals and Alloys
by Atomic Absorption Spectrometry
Non-Flame Methods

Element	Expected Conc'n. (ppm)	Accuracy (%)	Eqpt. Req'd (a)	Time to Prepare Sample (hr)	Sample Size (g)	Detection Limit (μg/g)(c)	Cost$^{(b)}$ Per Analysis ($)	Com-ments	References
Hg	1,10,100	25,15,5	A	2-4	0.001-0.1	10^{-4}	40-60	(d)	37,39,40,53
Be	"	"	B	2-4	0.001-0.1	10^{-6}	40-60	(d)	5,26,33
Cd	"	"	B or C	2-4	0.001-0.1	10^{-8}	40-60	(d)	33,39,60
As	"	"	C	2-4	0.001-0.1	10^{-4}	40-60	(d)	39,60,63
V	"	"	C	2-4	0.001-0.1	10^{-3}	40-60	(d)	36,60,63
Mn	"	"	B or C	2-4	0.001-0.1	10^{-6}	40-60	(d)	33,34,36,60
Ni	"	"	B or C	2-4	0.001-0.1	10^{-5}	40-60	(d)	33,34,36,60
Sb	"	"	B or C	2-4	0.001-0.1	10^{-5}	40-60	(d)	60,63
Cr	"	"	B or C	2-4	0.001-0.1	10^{-5}	40-60	(d)	34,60,63
Zn	"	"	B or C	2-4	0.001-0.1	10^{-6}	40-60	(d)	5,36,60,63
Cu	"	"	B or C	2-4	0.001-0.1	10^{-6}	40-60	(d)	5,36,60,63
Pb	"	"	B or C	2-4	0.001-0.1	10^{-5}	40-60	(d)	33,34,36,60
Se	"	"	B or C	2-4	0.001-0.1	10^{-4}	40-60	(d)	35,39,60,63
B	"	"	B	2-4	0.001-0.1	10^{-3}	40-60	(d)	36,60
F	No information.								
Li	"	"	B or C	2-4	0.001-0.1	10^{-4}	40-60	(d)	5,60
Ag	"	"	B or C	2-4	0.001-0.1	10^{-7}	40-60	(d)	34,36,39,60
Sn	"	"	B or C	2-4	0.001-0.1	10^{-5}	40-60	(d)	60
Fe	"	"	B or C	2-4	0.001-0.1	10^{-5}	40-60	(d)	33,60,63
Sr	"	"	B or C	2-4	0.001-0.1	10^{-5}	40-60	(d)	36,57,60,63
Na	"	"	B or C	2-4	0.001-0.1	10^{-4}	40-60	(d)	60,63
K	"	"	B or C	2-4	0.001-0.1	10^{-4}	40-60	(d)	5
Ca	"	"	B or C	2-4	0.001-0.1	10^{-5}	40-60	(d)	39,60,63
Si	"	"	B	2-4	0.001-0.1	10^{-6}	40-60	(d)	36,60,63
Mg	"	"	B or C	2-4	0.001-0.1	10^{-6}	40-60	(d)	33,60,63
U	No information.								
Th	No information.								

(a) AAS plus A = cold vapor method; B = carbon furnace; C = tantalum ribbon.
(b) Costs include nontechnical personnel skilled in AAS analyses.
(c) Separation and preconcentration required.
(d) Molecular scatter, background correction required.

Table 4. Analysis of Slurry Streams and Process Streams by Atomic Absorption Spectrometry Flame Methods

Element	Expected Conc'n. (ppm)	Accuracy (%)	Eqpt. Req'd (a)	Time to Prepare Sample (hr)	Sample Size (g)	Detection Limit (μg/g)	Cost[b] Per Analysis ($)	Comments	References
Hg	1,10,100	25,15,5	A	2-4	1-5	1	50-100		53
Be	"	"	B	2-4	0.1-1	0.5	50-100	(c)	7,49,55
Cd	"	"	C	2-4	0.01-1	0.1	50-100	(c)	50,55
As	"	"	D	2-4	0.1-1	0.2	50-100	(c)	7,55
V	"	"	B	2-4	0.1-1	0.6	50-100	(c)	7,55
Mn	"	"	C	2-4	0.1-1	0.1	50-100		24,27
Ni	"	"	C	2-4	0.1-1	0.1	50-100	(c)	7,27
Sb	"	"	A	2-4	0.1-1	0.1	50-100	(c)	7,24
Cr	"	"	B	2-4	0.1-1	0.5	50-100	(c)	24,27
Zn	"	"	C	2-4	0.1-1	0.1	50-100	(c)	24,27,50
Cu	"	"	C	2-4	0.1-1	0.2	50-100	(c)	24,27
Pb	"	"	C	2-4	0.1-1	0.2	50-100	(c)	24,27,55
Se	"	"	A	2-4	0.1-1	0.2	50-100	(c)	54
B	10,100	15,5	B	2-6	1-5	10	50-100		48,55
F	No information.								
Li	1,10,100	25,15,5	C	2-4	0.01-1	0.01	50-100		7
Ag	"	"	C	2-4	0.1-1	0.2	50-100	(c)	55
Sn	"	"	A	2-4	1-5	1	50-100	(c)	24,50
Fe	"	"	C	2-4	0.1-1	0.1	50-100	(c)	24,27
Sr	"	"	C	2-4	0.1-1	0.1	50-100	(c)	55
Na	"	"	C	2-4	0.01-.1	0.01	50-100		7
K	"	"	C	2-4	.01-.1	0.01	50-100		7
Ca	"	"	B	2-4	0.1-1	0.1	50-100	(d)	7
Si	10,100	15,5	B	2-4	1-5	1	50-100		7
Mg	1,10,100	25,15,5	C	2-4	0.1-1	0.1	50-100	(e)	55
U	10,100	15,5	B	2-4	1-5	10	50-100		7
Th	No information.								

(a) AAS plus oxidants and fuels: A=Ar+H_2; B=$N_2O+C_2H_2$; C=Air+C_2H_2; D=Air+H_2.

(b) Costs include nontechnical personnel skilled in AAS analyses.

(c) Separation and preconcentration required for 1 ppm.

(d) Ionization suppressor required.

(e) Releasing agent required ($LaCl_3$).

Table 5. Analysis of Coal, Oil, Organometallics
by Atomic Absorption Spectrometry
Flame Methods

Element	Expected Conc'n. (ppm)	Accuracy (%)	Eqpt. Req'd (a)	Time to Prepare Sample (hr)	Sample Size (g)	Detection Limit (μg/g)	Cost$^{(b)}$ Per Analysis ($)	Com-ments	References
Hg	1,10,100	25,15,5	A	2	1-5	1	20-40		6,38,53
Be	"	"	B	2-4	0.1-1	0.3	40-60	(c)	6,11
Cd	"	"	C	2	0.01-1	0.1	20-40	(c)	6,35
As	"	"	A	2-4	0.1-1	0.2	20-40	(c)	12,13,47
V	"	"	B	2	0.1-1	0.6	20-40	(d)	6,14
Mn	"	"	C	2	0.1-1	0.1	20-40	(d)	6,14,17,38
Ni	"	"	C	2	0.1-1	0.1	20-40	(d)	6,14,16,39
Sb	"	"	A	2	0.1-1	0.1	20-40	(c)	15
Cr	"	"	B	2-4	0.1-1	0.5	20-40	(d)	6,19,28,31
Zn	"	"	C	2	0.1-1	0.1	20-40	(d)	6,20,35
Cu	"	"	C	2	0.1-1	0.2	20-40	(c)	28,31,32,35
Pb	"	"	C	2	0.1-1	0.5	20-40	(c)	28,32,35
Se	"	"	A	2-4	0.1-1	0.2	20-40	(c)	13,47
B	10,100	15,5	B	2-4	1-5	10	50-100		11,19,48
F	No information.								
Li	1,10,100	25,15,5	C	2	0.1-1	0.01	20-40		6,20,45
Ag	"	"	C	2	0.1-1	0.3	20-40	(e)	20,21,31,32
Sn	10,100	"	D	2-4	1-5	1	40-60		6,28
Fe	1,10,100	"	C	2	0.1-1	0.1	20-40		19,28,31,32
Sr	"	"	C	2	0.1-1	0.1	20-40	(f)	6,7,56
Na	"	"	C	2	0.01-.1	0.1	20-40		6,19,28
K	"	"	C	2	0.01-.1	.05	20-40		6,7,56,64
Ca	"	"	C	2	0.1-1	0.1	20-40	(f)	38,58,64
Si	10,100	"	B	4-6	1-5	1	50-100		6,20,28,42
Mg	1,10,100	"	C	2	0.1-1	0.1	20-40	(f)	6,20,21,64
U	10,100	"	B	2-4	1-5	10	50-100		7
Th	No information.								

(a) AAS plus oxidants and fuel: A=Ar+H_2; B=N_2O+C_2H_2; C=Air+C_2H_2; D=Air+H_2.
(b) Costs include nontechnical personnel skilled in AAS analyses.
(c) Separation and preconcentration required for 1 ppm.
(d) Ionization suppressor required.
(e) Molecular scatter interferences.
(f) Releasing agent required ($LaCl_3$).

Table 6. Analysis of Coal, Oil and Organometallics by Atomic Absorption Spectrometry Non-Flame Methods

Element	Expected Conc'n. (ppm)	Accuracy (%)	Eqpt. Req'd (a)	Time to Prepare Sample (hr)	Sample Size (g)	Detection Limit (μg/g)	Cost(b) Per Analysis ($)	Comments	References
Hg	1,10,100	25,15,5	A	2-4	.001-0.1	10^{-4}	40-60	(c,d)	18,37,39,40, 52,53
Be	"	"	B	"	"	10^{-6}	"	"	60,63
Cd	"	"	B or C	"	"	10^{-8}	"		39,63
As	"	"	C	"	"	10^{-4}	"	"	47,60,63
V	"	"	C	"	"	10^{-3}	"	"	36,63
Mn	"	"	B or C	"	"	10^{-6}	"	"	5,60,63
Ni	"	"	B or C	"	"	10^{-5}	"	"	18,60,63
Sb	"	"	B or C	"	"	10^{-5}	"	"	60,63
Cr	"	"	B or C	"	"	10^{-5}	"	"	60,63
Zn	"	"	B or C	"	"	10^{-6}	"	"	39,60,63
Cu	"	"	B or C	"	"	10^{-6}	"	"	18,60,63
Pb	"	"	B or C	"	"	10^{-5}	"	"	18,39,63
Se	"	"	B or C	"	"	10^{-4}	"	"	5,39,47
B	"	"	B or C	"	"	10^{-3}	"	"	60
F	No information.								
Li	1,10,100	25,15,5	B or C	"	"	10^{-4}	"	"	5,60
As	"	"	B or C	"	"	10^{-7}	"	"	5,18,63
Sn	"	"	B or C	"	"	10^{-5}	"	"	60
Fe	"	"	B or C	"	"	10^{-5}	"	"	5,18,36
Sr	"	"	B or C	"	"	10^{-5}	"	"	60
Na	"	"	B or C	"	"	10^{-4}	"	"	5
K	"	"	B or C	"	"	10^{-4}	"	"	5
Ca	"	"	B or C	"	"	10^{-5}	"	"	5,39,63
Si	"	"	B	"	"	10^{-6}	"	"	36,63
Mg	"	"	B or C	"	"	10^{-6}	"	"	5,18,19,63
U	No information.								
Th	No information.								

(a) AAS plus: A=cold vapor method; B=carbon furnace; C-tantalum ribbon furnace.
(b) Costs include nontechnical personnel skilled in AAS analyses.
(c) Separation and preconcentration required to attain stated detection limits.
(d) Molecular scatter, background correction required.

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CHAPTER 6

ABSORPTION SPECTROPHOTOMETRY

R. W. Burke

1. INTRODUCTION

For the past forty years, absorption spectrophotometry has played a major role in the analysis of important industrial and research materials. Numerous factors have been responsible for the popularity of this technique. Foremost among these are: (1) its modest apparatus requirements, (2) the possibility of its use by skilled technicians, (3) its good sensitivity and (4) its high accuracy.

Several points should be clearly understood, however, before discussing specific applications of this technique to the analysis of the wide variety of materials which are currently of interest to EPA. First, absorption spectrophotometry is, for all practical purposes, a wet-chemical technique. Samples must therefore always be dissolved before an analysis can be made. Depending on the type and complexity of the matrix, sample dissolution can be, and frequently is, the limiting step in the analytical procedure. This deficiency, however, is common to all wet-chemical techniques and is best overcome by the analyst's experience. A second drawback of absorption spectrophotometry is that it is primarily a single element technique. Consequently, it is not suited for quick, survey-type, analyses. Finally, the technique is generally not specific and, as a rule, its successful application requires that the element of interest be separated from the remainder of the matrix. Such a requirement may be considered both a weakness and a strength. For example, separations may be tedious and small losses of the desired constituent may occur. Also, interfering elements may not be completely eliminated. On the other hand, if satisfactory separations can be made - and this is more often true than not - the effect of foreign elements is eliminated, and the spectrophotometric method becomes essentially an absolute one. This is often not the case with more sophisticated instrumental techniques in which chemical separations generally are not made. The accuracy of the latter methods depends on the availability of well characterized standards whose compositions closely approximate that of the materials being analyzed. In absorption spectrophotometry, suitable standards are prepared from high purity elements or compounds which are readily available commercially.

2. ANALYSIS OF SPECIFIC MATERIALS

Tables 1 and 2 summarize the relevant information on the possible spectrophotometric determination of some twenty-one elements in fly ash, incinerator particulates, coal, oil, ores, minerals, metals, alloys, organometallics, slurry streams and flotation feeds. Most of the references cited are not matrix oriented, but instead, deal specifically with the isolation, preconcentration and spectrophotometric determination of a particular element. This approach was necessary for two reasons: (1) there are relatively few references in the literature dealing with the spectrophotometric analyses of the above matrices and (2) those that were found employed for the most part, at least from the viewpoint of the research analyst, inferior methods. These findings are not surprising however, since widespread interest in the analysis of these types of materials has arisen only in the past few years. The lack of procedures is undoubtedly further accentuated by the fact that absorption spectrophotometry is primarily a single element rather than a survey technique.

The criteria used to divide the various matrices into the two general groups given in tables 1 and 2 were (1) their complexity and (2) their ease of dissolution. It is these same two factors which dictate the differences in accuracy and detection limits listed. Further examination of the two tables will show that a number of elements have been marked with an asterisk. These are the elements which are considered best determined by absorption spectrophotometry.

Perhaps the most variable parameters in these tables relate to the time and cost of an analysis. The figures given were taken largely from personal experience and are the best estimates for a "one-shot," single element determination. These costs can undoubtedly be substantially reduced, perhaps even tenfold, by determining several elements on the same sample and/or by determining the same element simultaneously in a number of samples of similar material.

As already mentioned, one of the advantages of absorption spectrophotometry is its modest apparatus requirement. This is indeed true since, for about $5,000, a laboratory can become well equipped to analyze for most of the elements listed. In spite of its relatively low cost, spectrophotometric instrumentation is quite rugged with downtime perhaps averaging no more than 1 percent.

3. CONCLUSIONS

The primary purpose of this chapter has been the delineation of state-of-the-art procedures for the spectrophotometric determination of some twenty-one elements in fly ash, incinerator particulates, coal, oil, ores, minerals, metals, alloys, organometallics, slurry streams and flotation feeds.

The majority of the references cited deal with the fundamental chemistry involved in the selective separation and color-forming reactions of these elements. By employing highly selective separations, the accuracy of the measurement should be scarcely affected by the nature of the matrix being analyzed, provided adequate dissolution procedures are used.

In all of the methods referred to above, solvent extraction has invariably been the method of choice when separations are necessary. This method is the most widely used technique because of its simplicity and speed. By utilizing apparatus no more complicated than a separatory funnel and requiring at most a few minutes to perform, solvent extraction offers a superior approach to performing elemental analyses of these types of materials. They are especially useful in absorption spectrophotometry since separation, preconcentration, and, frequently, color development can be performed in the same operation.

The greatest impact that absorption spectrophotometry can make in the near future appears to be in the areas of standards development and analysis. However, once more definitive specifications and tolerances are established, spectrophotometry should play an important role in the quality control and routine analysis of these materials.

Spectrophotometric procedures have been heavily automated in the clinical field, and commercially available auto-analyzers are highly popular. This suggests strongly that the same can be done for industrial applications, with attendant savings in costs and convenience for routine trace element determinations of the future.

Table 1. Analysis of Coal, Oil, Organometallics, Metals, and Alloys by Absorption Spectrophotometry(a)

Element(b)	Expected Conc'n. (ppm)	Accuracy (%)	Sample Size (g)	Expected Conc'n. (ppm)	Accuracy (%)	Sample Size (g)	Detection Limit(c) (μg)	Inter-ferences	References
Hg	1-10	25	1.0	100	5	0.1	0.1	Cu, Ag	1-5
Be*				1-100	5	0.1	0.1		6,7
Cd*	1-10	15	1.0	100	5	0.1	0.1	Co	8
As*	1-10	25	1-2	100	5	0.1	0.5		1A,9,10
V				10-100	15	1-2	5		1B,2B,11
Mn*	1-10	25	1-2	100	5	0.1	5		12,13
Ni*	1-10	5	1-2	100	5	1.0	0.1	Cu, Co	3B,14,15
Sb*				1-100	5	0.1-0.5	0.1	Au, Tl	16,17
Cr	1-10	25	1-2	100	5	0.1	0.5		18
Zn	1-10	15	1.0	100	5	0.1	0.1		2A,3A,19,20
Cu*				1-100	5	0.1	0.1	Hg, Pd	3B,21,22
Pb	1-10	15	1.0	100	5	0.1	0.1		4B,23
Se*				1-100	15	0.1	0.1	Mo, V	24,25,26
B*	1-10	15	1.0	100	5	0.1	0.1		27-33
F				10-100	15	1.0	2		4A,34,35,36
Ag	1-10	15	1.0	100	5	0.1	0.5		37,38
Sn*	1-10	25	1-2	100	5	0.1	1		39,40,41,42
Fe*	1-10	15	1.0	100	5	0.1	0.1		6B,43,44
Si*	1-10	25	2-5	100	5	0.5	0.5		45,46
U				10-100	15	1.0	2		47,48,49
Th				10-100	15	1.0	2		50,51

(a) Precision u.v.-visible spectrophotometer; skilled technician requires 0.5 - 4 hours for sample preparation; cost $50 - 100 per sample.

(b) Method recommended particularly for elements marked with an asterisk; not recommended for determination of Li, Sr, Na, K, Ca, Mg.

(c) To convert μg to ppm divide the detection limits (μg) by the sample weights (g).

Table 2. Analysis of Fly Ash, Ores, Minerals, Incinerator Particulates, Slurry Streams, Process Feeds by Absorption Spectrophotometry(a)

Element(b)	Expected Conc'n. (ppm)	Accuracy (%)	Sample Size (g)	Expected Conc'n. (ppm)	Accuracy (%)	Sample Size (g)	Detection Limit(c) (μg)	Interferences	References
Hg	10	25	1.0	100	5	0.1	2	Cu, Ag	1-5
Be*	1-10	25	1.0	100	5	0.1	0.5		1C,6,7
Cd*	10	15	1.0	100	5	0.1	1	Co	8
As*	1-10	25	1-2	100	5	0.1	0.5		1C,9,10
V	10	25	1-5	100	5	1-5	5		11
Mn*	10	25	1.0	100	5	0.1	5		12,13
Ni*	1-10	25	1.0	100	5	0.1	0.5	Cu, Co	14,15
Sb*	1-10	25	1-2	100	5	0.1	0.5	Au, Tl	16,17
Cr	10	25	1-5	100	5	1-5	2		18
Zn	10	25	1-2	100	5	1-2	2		19,20
Cu*	1-10	25	1.0	100	5	0.1	0.5	Hg, Pd	21,22
Pb	10	25	1.0	100	5	0.1	2		23
Se*	1-10	25	1.0	100	5	0.1	0.5	Mo, V	3C,24,25,26
B*	10	25	1.0	100	5	0.1	2		27-33
F	--	--	--	10-100	25	1	2		34,35,36
Ag	10	25	1.0	100	5	0.1	2		37,38
Sn*	10	25	1-2	100	5	0.5	2		39-42
Fe*	10	25	1.0	100	5	0.1	1		43,44
Si*	1-10	25	2-5	100	5	0.5	0.5		45,46
U				10-100	25	1-2	5		47,48,49
Th				10-100	25	1-2	5		50,51

(a) Precision u.v.-visible spectrophotometer; skilled technician requires 2-8 hours for sample preparation; cost $100-200 per sample.

(b) Method recommended particularly for elements marked with an asterisk; not recommended for determination of Li, Sr, Na, K, Ca, Mg.

(c) To convert μg to ppm divide the detection limits (μg) by the sample weights (g).

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CHAPTER 7

ATOMIC EMISSION SPECTROSCOPY

Danold W. Golightly

1. INTRODUCTION

Atomic emission spectra of the elements have long provided a powerful means for multi-element, chemical trace analysis. The capabilities of optical emission spectrometric analysis have improved with the increasing demands of our developing technological age and the growing awareness of the contribution of trace concentrations of many elements to environmental contamination.

A modern perspective of the state-of-the-art for trace and sub-trace analysis by optical emission spectrometry (OES) can be obtained from several books (1B-6B) and reviews (1R-8R) on the subject. However, neither state-of-the-art nor details of techniques are simple to elucidate concisely. This chapter summarizes the most recent techniques for OES analysis for 27 elements in the matrices: fly ash, coal, oil, ores, minerals, metals, alloys, organometallics, incinerator particles, slurry streams, and feeds and sediments in flotation processes.

A. Optical Emission Sources

The basic sensitivity (change in analyte signal per unit change in analyte concentration) of optical emission spectrometry is a complex function of analyte element, sample matrix, emission source, detector(s), and spectrometer optics. Thus, elements that have low excitation potentials for resonance lines and little tendency to form stable or non-volatile compounds are readily detected and have good sensitivity in most plasma-like discharges. The importance of compound formation and volatility are most dramatically incurred with the classical direct-current arc discharge.

DC Arc

The common d-c arc customarily is described as a source more sensitive, but less precise, than spark-type electrical discharges (with electrode configurations: rotating disk, porous cup, vacuum cup, etc.). However, detectability of elements in solid and powdered matrices is more a function of the large (10-20 mg) undiluted (usually only slightly diluted with graphite or buffers) sample quantity that is vaporized into the arc discharge rather than inherent sensitivity for all elements. Typical detection limits for elements in silicate ores (non-volatile matrix) are listed in table 1, column 1 (1). Spectroscopic buffers that control volatilization of solid compounds and stabilize excitation conditions in the arc plasma enable considerable improvement in spectrographic detectability. Harvey (2) has provided tabulated empirical data that show the importance of matrix and buffers. Harvey's detection limits for elements in a Li-salt buffer are shown in table 1, column 2.

Further improvements in detectability of the elements in spectra and d-c arcs have come from the use of rare-gas atmospheres (usually Ar) that enclose the discharge (3, 4, 5, 6, 7). Atmospheres of argon, or argon mixed with a reactive gas (such as oxygen), have made possible the improved detectability illustrated in table 1, column 3.

Most recently, Gordon and Chapman (8) have reported on a controlled-atmosphere, d-c arc method that uses AgCl as a common matrix. Their method, which is similar to residue methods discussed later in this chapter, requires a solution of the sample, but enables automated analyses for µg-quantities of analytes and good precision. Minimum detectable quantities (8) for elements of interest are illustrated in table 1, column 4. Hambidge (9) adapted Gordon's method for analysis of chromium in blood, hair and urine. Serum aliquots of 0.2 ml provided 1-7 ng quantities of chromium that could be determined with coefficients of variation of about 6 percent.

Sparks and AC Arcs

Discharges characterized as high-voltage sparks and interrupted arcs generally provide means for measurements more precise than d-c arcs. However, solutions or residues from solutions are required. Solutions assure homogeneity and a convenient means for addition of internal references not common to d-c arc powder methods. Some typical detection limits by porous cup and rotating disk spark methods are given in table 1, column 5 (10-13a, 13b).

Dilute solutions are particularly amenable to analysis by the copper-spark or graphite-spark technique. This method was first described by Gerlach and Riedl (14) in 1934, and later examined thoroughly by Fred, Nachtrieb and Tomkins (15) [for more recent descriptions, see references 16, 17, 18]. A residue is produced on flat-surfaced impermeable electrodes by vaporization of a small volume of solution. This residue then is sampled directly by a spark discharge. The method is sensitive and capable of high precision (1-3 percent). Typical minimum detectable quantities are shown in table 1, column 6. The presence of large amounts of matrix material in the residue is detrimental to detectability and precision, however, chemical separations, such as extraction, ion exchange, or electrodeposition, possibly can be used to remove matrix elements and enrich (or preconcentrate) impurity elements of interest.

Duffendack et al. (19, 20) have utilized a high-voltage a-c arc, rather than a spark, for analysis of residues on graphite electrodes. High sensitivity and good accuracy (19, 21) have been shown for this technique. More recently, Zhigalovskaya et al. (22, also see 22a, 22b) have described a short-pulse d-c technique that they found superior to the copper spark method in determining nanogram quantities of elements.

Hollow Cathode

Mention also must be made of the hollow-cathode discharge. The hollow cathode provides intense line spectra of the elements and enables analysis of small samples. In addition, the source makes possible convenient analyses for the halogens and other elements with high excitation potentials. The method is essentially a residue technique because solid sample is placed or electrodeposited within the hollow cathode. Some typical absolute detection limits (23, also see 23a, 23b) are given in table 1, column 7. Matrix effects are frequently incurred with this source, especially if the sampling mechanism is not ion sputtering alone. The hollow cathode lamp has been successfully applied to the analysis of trace elements in steels (23c) and non-conducting materials (23d).

Flame Emission

Flame atomic emission spectrometry is an important analytical technique that too frequently is overlooked in searches for analytical methods. Nearly 70 elements can be determined with flames that are in common use: nitrous oxide-acetylene, oxygen-acetylene, oxygen-hydrogen, etc. Some detection limits from oxygen-acetylene flames (24) are surveyed in table 1, column 8.

From among the various microwave discharges, capacitative-coupled and inductively coupled flame-like plasmas, the induction-coupled argon plasma appears to be a source that provides stable, bright spectra and thus, good detectability for many elements. Table 1, column 9 summarizes detection limits from this source (25, 26).

B. Chemical Preconcentration

The key to OES analysis of many elements approaching part-per-billion concentrations is preconcentration (or enrichment) of impurities. General methodology and precautions have been described by Thiers (27), Minczewski (28), Mizuike (29), and Lighty and Currier (30).

The techniques of most importance to removal of impurities from a matrix and concentration are liquid-liquid extraction, ion-exchange and electrodeposition. Some typical details and commentary on application of these approaches to optical emission spectrometry have been given by Lighty (30) and others (16, 27).

Recently, Jackwerth et al. have described DTPA complex exchange reactions (30a), coprecipitation of trace elements with thallium iodide, followed by extraction with DDTC (30b), enrichment of copper as the copper-cuprizone complex on silver bromide (30c), and trace enrichment by partial dissolution of matrices (30d) as sample manipulations preceding spectrochemical analysis.

2. APPLICATION TO MATERIALS OF ENVIRONMENTAL INTEREST

The twelve matrices, subjects of this report, can be separated into five groups for discussion. These groups, which assemble similar matrices, are:

A. Group 1 - Streams to and from Air Scrubbers

The liquids and solids collected in wet scrubbers can be analyzed by techniques long established by Kopp and Kroner (31a, 31b, 32a, 33a, p. 1010). Kopp and Kroner analyzed for Ag, Al, As, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Mo, Mn, Ni, P, Pb, Sr, V, and Zn in preconcentrated water samples by the rotating-disk high-voltage spark method. Concentrations from 0.01 to 100 μg/ml were determined on a direct-reading spectrometer. A volume of water evaporated (8 to 10 hrs) to 5 ml contained 20g of total solids/liter; the major portions of solids were salts of Ca, K, Mg, and Na. Concentration ranges for the various elements analyzed are shown in table 2, column 1. Four other methods are discussed in the paper (31a). These techniques and others (31c, 31d), for spectrometric water analysis should be directly applicable to analysis of water from wet scrubbers.

Haffty (32b) has described a residue method capable of detecting almost 60 elements in the ng/ml range. The technique has been applied to analysis of water sediments. Barnett (33a, p. 1001) has described a residue method for analysis of water. Concentration ranges are shown in table 2, column 2. The method is accurate (5-15 percent) and has a 1-2 percent coefficient of variation.

B. Group 2 - Metals and Alloys (Fe, Al, Cu, Pb, Zn)

Methods for spectrometric analysis of the metals Al, Cu, Fe, Pb and Zn are detailed in the ASTM Methods for Emission Spectrochemical Analysis (33a). Only metal constituents important to bulk metallurgical properties of these alloys are of concern in the ASTM methods. An example of elements and their concentration ranges determined in aluminum by the sensitive point-to-plane spark is given in table 2, column 3. These concentration ranges typify the concentrations of interest for analysis of alloys of copper (33a, p. 445), of iron (33a, p. 215), of lead (33a, p. 490), and of zinc (33a, p. 532). Balfour, et al. (33b) have developed a chemical preconcentration technique that enables emission spectrochemical analysis to be carried out for parts-per-million of Ag, As, Au, Bi, Cd, Ge, In, Mo, Pb, Sn and Tl in alloys of Al, Cr, Co, Fe, Ni and Ti. Killeen (33c) has used a dc-arc for analysis of trace elements in aluminum.

Tymchuck, et al. (34a, 34b) have found that Cu(OH)F is a good carrier for analysis of trace impurities, from volatile arsenic to refractory vanadium, in high-purity copper. For ppm and sub-ppm determinations, chemical preconcentration methods, defined by the specific problem, will be required.

Elwell and Scholes (35), Dozinel (36), Tolle (36a) and Publicover (36b) provide further information on spectrometric analysis for traces and minor constituents in copper and its alloys (see table 2, column 5). Four alloy steels are treated in a special technical publication of the British Iron and Steel Institute (37). Thornton (23c) has analyzed for traces in several iron-base alloys with a hollow-cathode lamp. Atwell and Golden (37a) have developed a carrier-distillation method for analysis of Pb, Bi and Sn in nickel-base alloys.

C. Group 3 - Ores, Minerals, and Sediments from Coal Flotation Processes

Typical standard methods for spectrochemical analysis of ores, rocks, and minerals (33a, p. 267, p. 958, p. 968, p. 982, p. 1027) are concerned with major constituents. Simultaneous multiple-element analyses for trace elements in minerals and rocks have been treated by Avni and Boukobza (48), Tennant and Sewell (49), Moal et al. (50), Schoenfeld (51), de Villiers et al. (52) and in ores by de Montleau (53). Shapiro (38a) recently has reviewed methodology for silicate rock analysis. Table 2, column 7 presents typical analyses of minerals.

Direct analysis of trace elements in ores can be accomplished with a buffer or with a carrier distillation method (34, 38). Also, there is an indication that boiler cap electrodes can provide improved d-c arc analysis for volatile elements, such as Hg, As and Zn (39, p. 239). Solution techniques for numerous ores require preliminary fusion with sodium peroxide or lithium metaborate. Collins (40) has analyzed waste waters from oil fields for B, Be, Fe, Mn and Sr by direct optical emission spectrography with a plasma-arc source.

D. Group 4 - Coal, Feeds to Coal Flotation Processes, Organometallics (formed by Combustion Processes)

The general subject of coal analysis for industry has been treated by Abernethy et al. (41a, 41b). Sharkey (42) has determined 53 elements in coal. Gibson and Ode (43) describe rapid methods for analysis of coal ash and similar matrices. Prior to solution of samples, a lithium metaborate fusion of the coal is accomplished in a platinum vessel (44, 45). Usual analytes and concentration ranges in the ashed residue are summarized in table 2, column 4 (43).

E. Group 5 - Fly Ash and Incinerator Particles

Principal constituents of fly ash are Si, Fe and Mg. This matrix is amenable to direct d-c arc analysis; or, after suitable fusion with lithium tetraborate or hydrofluoric acid dissolution, analysis can be performed with a rotating disk technique. Fusions with lithium borate flux have been used to reduce sample matrix effects (46, 47). Automated methods similar to those described by Tennard and Sewell (49c) for silicate minerals may be applicable to fly ash and incinerator particles.

3. COST (TIME) OF ANALYSIS

A. Survey Analyses

Qualitative and semiquantitative analyses can be made for all elements that have resonance lines or other relatively intense spectral lines within the limits of photographic plate response and transmission characteristics of the optics external to the spectrograph. A conventional d-c arc qualitative analysis provides an identification of major, minor, and trace constituents (up to 70 elements) typically in 10 mg of solid sample. Qualitative analyses also can be performed on liquid samples directly by spark methods or indirectly by residue methods. A semiquantitative analysis provides additional information on concentrations in terms of decade ranges defined by available standards and photographic exposures measured on a scanning microphotometer. This type of analysis is usually limited to 40 or 45 elements in a specific matrix material.

The cost for survey analysis is a composite sum of time (man-hours), and costs of electrodes, reference standards, buffers, gases for special discharge atmospheres, photographic plates and reagents. The time required for an analysis is the most significant of these cost contributors. Estimated times for qualitative and semiquantitative analyses are reviewed in table 4 for single sample multiple-element cases, and for multiple-sample multiple-element cases. All time estimates include the routine analysis; however, special samples may require up to several hours of pretreatment. The time required depends ultimately on the nature of the analysis and the complexity of the sample.

B. Quantitative Analyses

Quantitative analysis provides concentration information for traces and minor constituents that is typically accurate to within ± 5-10 percent of the true value. Reference standards such as the NBS Standard Reference Materials (SRM's) are necessary, and the physical and chemical similarity of standards and samples are crucial to the achievement of high accuracy.

Spectrographic methods require time-consuming microphotometry and graphical extrapolation methods. However, direct-reading (photoelectric) spectrometers can minimize or eliminate either or both of these time-consuming operations, thereby greatly reducing the time for quantitative measurements. These differences are reflected in the estimated times (costs) for quantitative analyses summarized in table 4.

Table 1. Summary of Spectrographic and Spectrometric Detection Limits[a]

Element	DC Arc Air (ppm)	DC Arc Li-Salt Buffer (ppm)	DC Arc Controlled Atmosphere (ppm)	DC Arc Reduced Pressure Argon (ng)	Porous Cup & Rotating Disk (ppm)	Spark Copper & Graphite (ng)	Hollow Cathode (ng)	Flame (μg/ml)	Argon Induction-Coupled Plasma (ng/ml)
Hg	3000	70	0.3	—	10	10	—	40	200
Be	1	1.5	0.005	0.1	0.02	0.2	0.03	1	—
Cd	10	15	0.08	20	0.2	20	30	6	30
As	100	800	0.1	—	3	100	—	50	100
V	1	0.8	5	—	0.2	1	—	0.3	6
Mn	1	0.6	0.03	1	0.02	0.2	0.03	0.1	—
Ni	30	3	0.1	3	0.5	1	1	0.6	6
Sb	100	80	0.1	2	2	10	100	20	200
Cr	3	0.5	0.5	2	0.1	1	1	0.1	1
Zn	100	70	0.1	45	4	10	3	50	9
Cu	0.3	0.2	0.1	0.4	0.05	0.5	0.03	0.1	—
Pb	1	7	0.3	1	4	5	10	3	8
Se	—	—	500[b]	—	—	—	—	—	30
B	30	15	0.4	—	0.5	0.2	1	30	30
F	300	—	—	—	—	10	—	—	—
Li	30	20	500[b]	1	0.1	0.2	0.1	0.000003	—
Ag	0.1	0.8	0.001	—	0.01	0.5	0.03	0.3	20
Sn	3	15	0.1	7	2	—	10	4	300
Fe	30	5	0.4	0.3	0.2	2.5	3	0.7	5
Sr	3	0.2	5	—	0.06	50	—	0.004	0.02
Na	100	20	500[b]	7	35[b]	10	0.03	0.0001	—
K	2000	15	1000[b]	20	200[b]	10	10	0.003	—
Ca	1	0.1	0.01	—	0.01	10	—	0.005	—
Si	3	8	0.4	3	1	10	1	5	—
Mg	0.3	0.2	0.1	0.2	0.003	1	0.03	0.2	5
U	50	500	500	—	100	100	—	10	30
Th	100	50	500	—	10	50	—	150	3

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[a] Index to references in Table 3.

[b] Most sensitive line not used.

Table 2. Summary of Spectrographic and Spectrometric Analysis of Various Materials[a]

Element	Water Rotating Disk Method (ug/ml)	Water Residue Method (ug/ml)	Aluminum Spark-Emission (%)	Coal Ash (Major Constituents)[b] (%)	Copper, Globular Arc (ppm)	Minerals, Phosphate Rock (ppm)	Minerals, Powders (ppm)
Hg	—	—	—	—	0.3-3	10-400	—
Be	0.005-1.4	0.6-30	0.001-1	—	0.01-0.2	10-400	1-6
Cd	0.2-20	6-30	0.001-2	—	0.1-1	10-400	5-6
As	4-80	—	—	—	3-40	10-400	1-2
V	2-40	1.5-30	0.001-0.05	—	0.1-1.5	10-400	20-90
Mn	0.1-20	1.5-3,000	0.001-8	—	0.1-0.8	10-400	200-1500
Ni	0.5-40	1.5-30	0.001-10	—	2-40	10-400	1-2500
Sb	—	—	—	—	2-40	10-400	0.6-1.2
Cr	0.2-40	1.5-30	0.001-4	—	0.2-3	10-400	8-400
Zn	0.5-80	90-3,000	0.001-10	—	0.5-10	10-400	40-700
Cu	0.2-40	0.3-300	0.001-30	—	—	10-400	13-8000
Pb	2-40	1.5-30	0.002-0.7	—	1-15	10-400	6-460
Se	—	—	—	—	—	—	—
B	0.1-20	1.5-300	0.001-0.05	—	0.01-0.3	10-400	—
F	—	—	—	—	—	—	—
Li	—	—	—	—	0.2-10	10-400	—
Ag	0.1-20	0.15-30	0.001-5	—	1-20	10-400	2.6
Sn	—	3-30	0.001-7.5	—	0.2-5	10-400	2.5-32
Fe	0.2-80	1.5-3,000	0.001-4	1-23	1-12	10-400	1%-25%
Sr	0.2-40	0.3-300	—	—	—	10-400	70-570
Na	—	—	0.001-0.05	0.3-11	1-15	10-400	—
K	—	—	—	0.6-1.4	—	10-400	—
Ca	—	—	0.001-0.2	4-21	0.5-5	—	100-9%
Si	—	—	0.001-14	14-41	—	—	15-41
Mg	—	—	0.001-11	0.8-5.5	0.1-1	10-150	0.07%-4.3%
U	—	—	—	—	—	0.5-400	0.5-2400
Th	—	—	—	—	—	50-400	2.5-300

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[a] Index to references in Table 3.
[b] Elements reported as oxides.

Table 3. Index to Emission Spectroscopy References

Column in Table 1	Spectrographic and Spectrometric Emission Sources	References
1	DC Arc in Air	1
2	DC Arc, Li Salt Buffer	2
3	DC Arc, Controlled Atmosphere	3,4,5,6,7
4	DC Arc, Reduced Pressure Argon	8
5	Spark, Porous Cup Rotating Disk	10,11,12,13
6	Spark, Copper and Graphite	15,16,17,18
7	Hollow Cathode	23
8	Flame	24
9	Argon Induction-Coupled Plasma	25

Column in Table 2	Spectrographic and Spectrometric Analysis of Various Materials	References
1	Water, Rotating Disk Method	32a
2	Water, Residue Method	32b, 33a
3	Aluminum, Spark Emission	33a, 33b
4	Coal Ash	45
5	Copper, Globular Arc	36b
6	Minerals and Phosphate Rocks	48
7	Minerals and Powders	52

Table 4. Estimates of Time Required for Several Types of Spectrographic and Spectrometric Analyses.

Type of Analysis	Number[(a)] of Samples	Number of Elements	Total Time (Hr.)	Time/Element Analysis (Min.)	Comments
Qualitative, Spectrographic	1	25	1.5	2-3	Solids, Powders, or Liquids.
	15	25	4	0.5-1	
Semiquantitative, Spectrographic	1	25	4	8-12	Solids or Powders. All samples of like matrices.
	12	25	8	1-3	
Quantitative, Spectrographic	1	1	2	120	Solids, Powders. All samples of like matrices.
	1	25	5	10-15	
	12	25	12	2-4	
Quantitative,	1	1	0.25	15	Solids, Powders, or Liquids.
Spectrometric	1	25	4	10	Direct-Reading Spectrometer with Intensity Ratio Output.
	12	25	6	1-3	
	12	25	0.25	0.05 (3 Sec.)	Direct-Reading Spectrometer with Dedicated Computer and Automatic Printout in Predetermined Format.

(a) For spectrographic analysis, this is the number of exposures that can be conveniently put on a pair of photographic plates in a spectrograph camera.

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CHAPTER 8

VOLTAMMETRY (POLAROGRAPHY)

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1. INTRODUCTION

Voltammetry (polarography) is a well known analytical technique that has considerable potential for environmental analysis. While best known for the determination of trace metals, it can be applied to the determination of some non-metals and to organic compounds as well. In fact, any substance that can be electro-oxidized or reduced in solution is potentially determinable by voltammetry.

Attractive features of voltammetry include high sensitivity, good selectivity, moderate cost of instrumentation, and the ability to determine several constituents in the same solution. Modern instrumentation has improved polarography with respect to sensitivity, selectivity, and ease of operation. Accordingly, it is surprising that the technique has not found more extensive use in environmental analysis.

In this chapter, the voltammetric techniques of analytical importance are described, chemistry pretreatment and matrix effects are discussed, and some of the experience obtained at NBS is mentioned. In addition, applications to environmental pollution found in the literature are reviewed and estimates are given of the types of results which can be expected.

Background

With a conventional d.c. pen-recording polarograph and a dropping mercury electrode, solutions containing as little as 1 μg/ml (0.01 millimolar) can be analyzed. Accuracies of 2-5 percent are found, and when reduction potentials are separated by as much as 200 mV, a number of elements can be determined in the same solution.

The sensitivity and resolution of polarographic analysis have been greatly extended by the development of modern instrumentation such as square wave and pulse polarography by Barker and co-workers (1). Of these, pulse polarography has been used most often for analytical purposes, and instruments are commercially available. With this technique, short voltage pulses of increasing amplitude are applied to the mercury drop (or a suitable cathode) which is held at the initial potential, and the current is measured near the end of the drop growth. For the differential pulse technique, short voltage pulses of constant amplitude are applied against a linearly increasing background voltage. In both cases the charging current is allowed to decay before the measurement of the faradaic current. Only changes in current are measured; therefore, increased sensitivity is obtained. Concentrations as low as 10 ng/ml can be determined and peaks differing by only 40 mV can be resolved.

Polarographic capabilities have also been improved by the development of cathode ray polarography by Randles, with further improvements by Davis and co-workers (2). With this instrument a linear voltage sweep is applied, in either the anodic or cathodic direction, during the last two seconds of the life of a mercury drop which is mechanically detached every seven seconds. The peak resulting from the electro-oxidation (or reduction) of the species in question, and which is proportional to its concentration, is displayed and measured on a cathode ray tube or a fast recorder. Sensitivities of 10 to 50 ng/ml can be obtained and peaks differing by less than 100 mV can be resolved.

By use of dual cells, differential operation may be obtained with this polarograph. Electrodes are matched by cutting a capillary into two pieces of equal length and using the cut faces as the dropping orifices. The drop masses are equalized by adjustment of the heads of the two mercury columns immersed in portions of the same solution to give identical reduction peak heights for each cell. For subtractive polarography, the second cell contains the blank, and its signal is electrically subtracted from that of the first cell containing the sample, giving much better defined peaks and higher sensitivity. In the same way, interfering peaks may be minimized by putting a similar amount of the interfering ion or ions in the second cell.

The best polarographic precision obtainable, so far, can be achieved by using the second cell in the comparative mode of operation; that is, placing in it a very accurately known standard, similar in concentration to the sample which is in the other cell. The very small difference between the two is then amplified and measured. By this technique, standard deviations as low as 2 to 5 parts in 10,000 have been obtained (3, 4). This makes possible highly accurate determination of macro constituents on micro amounts of sample.

The highest polarographic sensitivity, ranging from 1 ng/ml to 1 pg/ml can be obtained by anodic stripping utilizing any of the newer instrumentation presently available. This technique involves plating onto a cathodic electrode for a fixed length of time at an appropriate potential, then applying a voltage scan in the anodic direction, measuring the increased peak current resulting from the oxidation of the ion or ions in question which were accumulated on the electrode. A variety of types of electrodes may be used - including hanging mercury drop (either extruded or plated onto platinum or gold), thin film and solid electrodes, such as composite mercury-graphite, glassy carbon, etc. Cathodic stripping, which is the reverse of the procedure described above, can be used for determination of anions.

2. APPLICATIONS TO ENVIRONMENTAL ANALYSIS

Voltammetric analysis requires that the substances of interest be dissolved and contained in an electrolyte of favorable composition. Proper selection of this supporting electrolyte can also minimize interferences in the case of complex mixtures.

For simplification, the 12 matrices of interest have been combined into three separate groups. In some respects this is an oversimplication, as any one of the matrices may require some individual consideration. These groupings have been based, not necessarily on the similarities of the matrix, but rather on the complexity of sample dissolution and of other chemical pretreatments which may be necessary before the instrumental measurement. Fly ash, coal, oil, organometallics, incinerator particulates, and minerals are grouped together, because in most cases the matrix consists of carbon, organic matter, and/or silica, all of which can be readily eliminated by wet ashing and nitric, perchloric and/or hydrofluoric acids, leaving the ion of interest in a soluble form. The minerals in a few cases may consist, instead, largely of a heavy metal matrix rather than silica, and in such cases should be classified with ores, metals, and alloys. For the first group of matrices, supporting electrolytes may be chosen so that few direct interferences will exist for most of the ions of interest. In some cases better accuracies may be obtained because of increased resolution after a simple separation such as solvent extraction.

For ores, metals, and alloys, supporting electrolytes may be chosen for the specific problem at hand so that few direct interferences exist; however, the matrix materials (such as iron, lead, or zinc, etc.) may have a reduction potential in the vicinity of the ion in question, and which in excessive concentrations could decrease the resolution so that separation may be advisable. Ferric iron is reduced fairly close to zero volts, in many supporting electrolytes; hence if it is the major constituent, it may swamp out trace amounts of other ions reduced near zero volts. It may be extracted by a variety of means such as chloroform - cupferron, isobutyl acetate, or methyl isobutyl ketone. A much simpler solution, however, is to treat it with a reducing agent such as ascorbic acid or hydroxylamine hydrochloride converting it to ferrous iron which is reduced at a much more negative potential.

Lead may be eliminated in most cases by the addition of sulfate. Subsequent filtration is not necessary as the precipitated lead sulfate may be allowed to remain in the solution. Iron, in most cases, cannot be removed as a matrix interferant in a similar manner by precipitation with base, because the iron hydroxide precipitate is a colloidal, gelatinous one which could occlude trace metals of interest.

The zinc matrix causes no interference in most cases, as its reduction potential is more negative than most of the ions of interest.

For slurry streams, feeds to/and from flotation processes, sediments in flotation processes, effluents and water in general, water, which may comprise the bulk of the matrix, can be removed simply by evaporation. The remainder of residual material will fall under the classification of one of the first two groups and it can be treated in a similar manner. The presence of calcium, or other alkaline earths or alkalis present no problems, as they are all reduced at a sufficiently negative potential to cause no interference with the ions of interest in this study.

Cadmium in air has been determined by a number of workers after collection on cotton or glass wool plugs, filter paper, electrostatic precipitators or impingers. Silverman (5) determined cadmium in dust and fumes using several of these collection techniques. After dissolution of the collected sample and oxidation of the organic material with nitric acid and hydrogen peroxide and evaporation to dryness, cadmium was measured polarographically at -0.63V in a supporting electrolyte containing ammonium hydroxide and potassium chloride. Other workers (6) have used an ammonium chloride - ammonium hydroxide or a 30 percent ammonium acetate supporting electrolyte, and have also determined copper and zinc at the same time.

Landry (7) determined lead and zinc in the atmosphere using cadmium and manganese as internal standards, in an ammonium chloride-ammonium hydroxide supporting electrolyte. Earlier workers (8) determined lead in 0.1N KCl by addition of a known amount of either zinc or cadmium as an internal standard. This method requires that zinc or cadmium not be present in the sample. Kito (9) determined lead in 50-1000 ml samples of air using a supporting electrolyte of potassium nitrate, glycine and nitric acid at a pH of 3.

Tetraethyl lead in air was determined by Khlopin (10) after absorption of about 0.5 cubic meter of air in castor oil containing a saturated solution of iodine in methyl alcohol. The mixture was digested with nitric acid and evaporated to dryness. The residue was dissolved in dilute hydrochloric acid and measured in a 30 percent calcium chloride solution. Khlopin (11) used the same supporting electrolyte for the determination of zinc, lead, copper, cadmium, manganese, and bismuth in air. He reports that all six elements may be determined simultaneously.

Urone and coworkers (12) have described a micromethod for the determination of chromium in dusts and mists. After suitable pretreatment, chromium was oxidized with hydrogen peroxide and measured in 1N sodium hydroxide. The limit of sensitivity was about 0.05 µg/ml in the final solution and the error was ±4 percent.

A method has been described for the determination of manganese, chromium, and iron in air in a triethanolamine-sodium hydroxide supporting electrolyte (13). Pines (14) used a similar supporting electrolyte and determined amounts down to 20 µg of manganese in air with coefficients of variation of 8.5 percent. For 500-800 µg of manganese, the coefficient of variation was 2.5 percent.

Babina (15) determined titanium in air after absorption in 0.5 M sulfuric acid or collection on a PVC filter. Potassium oxalate was used as a supporting electrolyte and the pH of the solution was adjusted to 3 - 3.5 with potassium hydroxide. Errors of ±6 percent were obtained, and more than 50 µg/ml of iron and 1 µg/ml of vanadium interfered.

Arsine in gas mixtures has been determined by utilization of its anodic wave in a supporting electrolyte of ethanol and ammonium nitrate (16). Phosphine and stibine give waves at the same potential, hence would interfere.

Particulates collected in laboratory air, suburban air, rural air, and industrial air have been analyzed at the National Bureau of Standards by cathode ray polarography for iron, copper, lead, and cadmium; all four elements could be measured concurrently without separations, after wet ashing (17,18). Bulk particulate matter under study as a possible standard reference material was readily analyzed for copper, lead, cadmium, and zinc in the same solution (19).

Metal organics including quinolates and cyclohexanebutyrates have been readily analyzed for copper, nickel, manganese, iron, zinc, lead, or cadmium, directly after dry or wet ashing of the sample (17, 20). Most of these determinations were at the major constituent level, hence the determinations required only a few mg. of sample. Cadmium at the 25 percent level was determined directly in cadmium cyclohexanebutyrate after dry ashing. Standard deviations of 0.15 percent were obtained using the double cell comparative method (18).

Iron, copper, nickel, lead and aluminum have been determined in lubricating oils at the 1-, 50-, and 500-ppm level respectively, after dry ashing. These mixtures had been prepared as possible standards for monitoring engine failure (21).

Glass, rocks, and soils have been readily analyzed by polarography. Iron, titanium and nickel have been determined at the 1-, 50-, and 500-ppm levels in a series of doped glass Standard Reference Materials (22), with standard deviations of about 1 to 2 percent. The results agreed very well with those found by several other techniques (23).

Iron, titanium, and nickel have been determined in lunar rocks and fine soil from the Apollo 14, 15 and 16 flights. All three elements can be determined in a single 5-mg sample. The iron values for the different samples ranged from 3.5 to 15 percent; titanium, from 0.3 to 1.3 percent; and nickel, from 100 to 400 ppm (24).

Polarography has been useful in the analysis and certification of several of the NBS botanical Standard Reference Materials which present many of the same analytical problems as organics and particulates. Iron, aluminum, lead, cadmium, bismuth and nickel are all readily determined in amounts ranging from 0.1 to 350 ppm (25).

A considerable portion of the polarographic work at NBS has been concerned with metal and alloy analysis; hence, the usefulness of polarography in this application is amply demonstrated (4, 17-21). It has been used for rapid identification and analysis of metals and alloys in very small amounts of sample, and it should be applicable to the analysis of particulates from slurry streams, sediments, and fly ash. Identification of corrosion products is another one of NBS experiences that has applications of environmental interest.

Complete compositional analyses have been made on samples as small as 90 µg in the case of thin films composed of antimony-bismuth, lead-tin-tellurium, nickel-chromium-aluminum-copper, and lead-selenium (17, 18, 20, 21).

Various types of effluents and water systems have proved to be amenable to polarographic analysis. Periodic analyses have been made of copper and zinc in the local water supply to evaluate its suitability for use in a proposed National Aquarium. Water samples (100-500 ml) were filtered, the organic material destroyed by acid treatment, and the samples evaporated to dryness. The residues were dissolved in dilute hydrochloric acid and the solutions made ammoniacal. Copper and zinc were determined concurrently on the cathode-ray polarograph from peaks appearing at -0.4 V and -1.2 V, respectively. By use of the sample sizes indicated, the method was applicable down to at least 5 ppb of copper and zinc.

Samples of water from the NBS reactor have been routinely monitored for several elements including copper, cadmium, lead, iron, and aluminum directly, with no separations, in amounts ranging from 0.6 to 200 ppb.

3. CONCLUSIONS

The examples discussed here demonstrate the applicability of polarography to trace element determination in materials similar to the matrices under consideration. Additional applications found in the literature are given in the Bibliography. Tables 1, 2, and 3 give a summary of sensitivities, accuracies and costs that can be expected for typical samples.' In many cases the sensitivities achieved could be significantly greater and the cost of analysis could be considerably less than those indicated in the tables, with the expenditure of a little effort to optimize methodology. The sensitivities indicated in the tables are in general poorer than those given in instrumentation discussions for pure solutions, because a realistic evaluation has been made on the basis of problems which can occur with real samples. One of the main limits to the sensitivity achievable on real samples is the magnitude of the blank (both from reagents and from the environment). If the blank can be kept to a low level, then higher sensitivity can be achieved.

The prices for commercial voltammetric instrumentation range from about $3,000 to $16,000. No additional equipment should be required other than that present in an ordinary chemical analytical laboratory.

A technician, well-trained in analytical manipulations, should be capable of performing most of the analyses, provided a detailed procedure is available. A competent electroanalytical chemist should be available for consultation.

Table 1. Analysis of Fly Ash, Coal, Oil, Organometallics, Incinerator Particulates, and Minerals by Polarography

Element[a]	Accuracy[b] (%)	Time to[c] Prepare Sample (hr)	Detection Limit (ppm)	Sample[d] Size (g)	Cost[c] Per Analysis ($)	Comments[e]
Cd	0.1-10	0.5	10 ppb	1	3	In interferes[f]
As	2-15	1	0.5	1	6	(f)
V	2-15	2	0.5	1	12	(f)
Mn	2-15	2	0.1	1	12	(f)
Ni	2-15	1	0.1	1	6	(f)
Sb	2-15	1	0.1	1	6	(f)
Cr	0.2-15	1	0.1	1	6	Pb,Zn interfere[f]
Zn	0.2-15	1	0.1	1	6	(f)
Cu	0.2-15	1	0.1	1	6	(f)
Pb	0.2-15	1	0.1	1	6	Tl interferes[f]
Se	2-15	2	1	1	12	(f)
Sn	0.5-15	2	0.5	1	12	(f)
Fe	0.2-15	1	0.1	1	6	(f)
U	0.2-15	2	0.2	1	12	(f)

(a) Polarography not often used for: Hg, Be, B, F, Li, Ag, Sr, Na, K, Ca, Si, Mg, Th.

(b) Accuracy range: standard deviation (%) at macro constituent level to standard deviation at detection limit, by differential polarography.

(c) Time & costs based on sets of six samples, single-element determinations. Costs are considerably less for multi-element determinations in the same sample.

(d) Sample size requirement for elemental determination at stated detection limits. Larger samples give lower detection limits; smaller samples required for more abundant elements.

(e) See text for equipment and manpower requirements.

(f) Interfering elements can be separated.

Table 2. Analysis of Ores, Metals, and Alloys by Polarography

Element[a]	Accuracy[b] (%)	Time to[c] Prepare Sample (hr)	Detection Limit (ppm)	Sample[d] Size (g)	Cost[c] Per Analysis ($)	Comments[e]
Cd	0.1-10	1	50 ppb	1	6	In interferes[f]
As	2-15	2	1	1	12	(f)
V	2-15	2	1	1	12	(f)
Mn	2-15	2	1	1	12	(f)
Ni	2-15	1	0.5	1	6	(f)
Sb	2-15	1	1	1	12	(f)
Cr	2-15	1	1	1	12	Pb,Cu interfere[f]
Zn	0.2-15	1	1	1	12	(f)
Cu	0.2-15	1	0.5	1	12	(f)
Pb	0.2-15	1	0.2	1	6	(f)
Se	2-15	2	5	1	12	(f)
Sn	2-15	2	1	1	12	(f)
Fe	0.2-15	1	1	1	12	(f)
U	0.2-15	2	1	1	12	(f)

(a) Polarography not often used for: Hg, Be, B, F, Li, Ag, Sr, Na, K, Ca, Si, Mg, Th.

(b) Accuracy range: standard deviation (%) at macro constituent level to standard deviation at detection limit, by differential polarography.

(c) Time & costs based on sets of six samples, single-element determinations. Costs are considerably less for multi-element determinations in the same sample.

(d) Sample size requirement for elemental determination at stated detection limits. Larger samples give lower detection limits; smaller samples required for more abundant elements.

(e) See text for equipment and manpower requirements.

(f) Interfering elements can be separated.

Table 3. Analysis of Slurry Streams, Sediments, Process Feeds, and Water by Polarography

Element[a]	Accuracy[b] (%)	Time to[c] Prepare Sample (hr)	Detection Limit (ppm)	Sample[d] Size (g)	Cost[c] Per Analysis ($)	Comments[e]
Cd	0.2-10	0.5	10 ppb	1	6	In interferes[f]
As	2-15	1	0.5	1	6	(f)
V	2-15	2	0.5	1	12	(f)
Mn	2-15	2	0.1	1	12	(f)
Ni	2-15	1	0.1	1	6	(f)
Sb	2-15	1	0.1	1	6	(f)
Cr	0.2-15	1	0.1	1	6	(f)
Zn	0.2-15	0.5	0.1	1	3	(f)
Cu	0.2-15	0.5	0.1	1	3	(f)
Pb	0.2-15	0.5	0.1	1	3	Tl interferes[f]
Se	2-15	2	0.5	1	12	(f)
Sn	0.5-15	2	0.5	1	12	(f)
Fe	0.2-15	1	0.1	1	6	(f)
U	0.2-15	2	0.1	1	12	(f)

(a) Polarography not often used for: Hg, Be, B, F, Li, Ag, Sr, Na, K, Ca, Si, Mg, Th.

(b) Accuracy range: standard deviation (%) at macro constituent level to standard deviation at detection limit, by differential polarography.

(c) Time & costs based on sets of six samples, single-element determinations. Costs are considerably less for multi-element determinations in the same sample.

(d) Sample size requirement for elemental determination at stated detection limits. Larger samples give lower detection limits; smaller samples required for more abundant elements.

(e) See text for equipment and manpower requirements.

(f) Interfering elements can be separated.

Table 4. Element Index to References for Table 1. Fly Ash, Coal, Oil, Organometallics, Incinerator Particulates and Minerals by Polarography

Element Determined	References to Bibliography A
Mercury	
Beryllium	
Cadmium	2,3,6,7,11,12,13,16,25,29,30,32,42,164
Arsenic	2,17
Vanadium	40
Manganese	2,17,25,30,32,34,35,36,43
Nickel	13,13a,18,164
Antimony	3,17
Chromium	15,32,36,46b,46c
Zinc	2,3,11-14,17,25,29,30,31,32,41-44,46c,164
Copper	2,3,8-14,16,25,30,42,46b,46c,164
Lead	2,3,12,13a,16,17,20-32,42,46b,164
Selenium	
Boron	
Fluorine	
Lithium	33
Silver	
Tin	37,46b
Iron	2,13a,17,18,36,46b,164
Strontium	
Sodium	1
Potassium	1
Calcium	
Silicon	
Magnesium	19
Uranium	38, 39
Thorium	
Reviews	45,46,46a

Table 5. Element Index to References for Table 2. Ores, Metals, and Alloys by Polarography

Element Determined	References to Bibliography B
Mercury	
Beryllium	
Cadmium	54,57,58,62,68,69,78,85,86,92,93,96-99,116,117, 121-123,126
Arsenic	47,52,71,81,83,95,100
Vanadium	
Manganese	51,53,100
Nickel	50,53,60,70,78,99,103,113,117
Antimony	47,53,69,70,78,82,90,94,99,119
Chromium	70,75
Zinc	51,55,62,66,75,77,78,80,86,92,98-100,103,104 110-113,116-118
Copper	48,55,59,62,68,69,70,72-75,78,84,86,91,94,99,100, 103,113-117,119,121,123,124
Lead	48,53,56-59,62,67,69,70,73,74,76-78,84,86,87,92-94, 99,100,103-105,114-116,119-121,125-127
Selenium	61,62,106
Boron	
Fluorine	
Lithium	
Silver	88
Tin	47,69,70,78,79,89,90,93,103,107,108,126,128,129
Iron	53,69,91,99,104,117,121,124
Strontium	
Sodium	
Potassium	
Calcium	
Silicon	
Magnesium	
Uranium	109
Thorium	
Thallium	49,65,85,122, 126,127
Tellurium	52,63,64,69, 70,106
Reviews	102,131,132

Table 6. Element Index to References for Table 3. Slurry Streams, Sediments, Process Feeds, and Water by Polarography

Element Determined	References to Bibliography C
Mercury	
Beryllium	
Cadmium	145,148,149,152,153,155,161-164,166, 180-183,186
Arsenic	140-143,186
Vanadium	161,177
Manganese	145,151,168
Nickel	152-155,161,163,166,168,177
Antimony	139
Chromium	177
Zinc	138,145,148,149,151-153,155,157,161, 163,164,166,167,178-184,186
Copper	137,145-157,163,165,166,181-183,186
Lead	137,145,148,149,152,153,155,156,158, 159,161-167,181,183
Selenium	170
Boron	
Fluorine	186
Lithium	135,186
Silver	
Tin	138,164,186
Iron	137,145,151,163,156
Strontium	
Sodium	133-135,186
Potassium	133,134
Calcium	133,134,177,186
Silicon	
Magnesium	133,134,136,177,186
Uranium	171-176,186
Thorium	
Bismuth	139,144,148,161,186
Reviews	185,186

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CHAPTER 9

POTENTIOMETRY (ION-SELECTIVE ELECTRODES)

Richard A. Durst

1. INTRODUCTION

Ion-selective electrodes, when applicable, provide one of the simplest analytical methods for measurement of the concentration of dissolved substances. Modern electronic potentiometers provide essentially direct readout in concentration units, independent of operator skill or judgment. When the substance of interest is already dissolved, it may be monitored automatically and continuously.

Selectivity is produced in an electrode by selection or suitable modification of the electrode membrane material. Thus the glass electrode which is highly selective for hydrogen ions and provides the best means for pH measurement, may be made responsive to other univalent cations by modification of the glass matrix. Selectivity for other ions is achieved by the use of electrodes incorporating solid membranes or by use of liquid ion-exchange membranes as electrodes. Background information on these and related matters will be found in the general references (1, 2).

General Considerations

Applicability to most of the sample matrices under consideration requires a pretreatment procedure involving sample dissolution and masking of interferences to provide an appropriate sample in solution form. In certain cases, process streams - including feeds, effluents, and slurries - may be monitored directly by electrode sensors with minimal pretreatment. Ion-selective electrodes are logarithmic sensors (emf output is proportional to the logarithm of the concentration) hence their response, i.e., precision, is constant over their entire dynamic operating range. Strictly speaking, the electrodes respond to ionic activities rather than concentrations. The latter, which is ordinarily the quantity of analytical interest, must be obtained by dividing the activity by the activity coefficient. This problem can be overcome by empirical calibration using solutions of known concentration. Dissolution of the sample in a medium of constant ionic environment is another procedure that has been used (1,2). Under ordinary laboratory conditions, an imprecision of approximately 1-5 percent is normal, while in plant or remote monitoring situations, 5-10 percent imprecision may be expected. Using titration procedures, which are usually more complex and time consuming than direct measurements, imprecisions on the order of 0.1 percent can be achieved. For routine analyses, automatic titrations and standard addition techniques using Gran plot end-point detection can result in rapid determinations while still retaining the higher accuracy and precision.

Manpower skills required to make electrode measurements are minimal once the analytical procedures are developed, however, sample preparation and pretreatment may be highly complex and require a technician trained in chemical manipulations such as wet ashing, separations, and dilution.

At the present time, there are over two dozen different kinds of commercially available ion-selective electrodes. Of these, almost half are suitable for the determination of elements of interest in this survey. The cost of these sensors ranges from $150 to $300, depending on type (i.e., solid-state, liquid ion-exchange, combination, etc.). Portable, battery-operated meters are available in the $100 to $500 range, while more sophisticated laboratory-based digital readout meters cost approximately $1,000. In addition, it is usually convenient to use a recorder ($300 to $2,000, depending on features) to monitor emf stability and plot titrations, although this accessory is not required. Other items such as stirrers, reagents, and glassware are usually trivial expenses. Thus, an ion-selective electrode measurement system can be acquired for as little as $300, or more typically, $1,000 to $2,000.

Analysis costs will depend on the number of samples to be analyzed, the pretreatment involved which depends on the matrix of the sample, and the accuracy and precision desired which determine the particular electrode procedure to be used, i.e., direct measurement, titration, addition technique, etc. In general, automated procedures can be developed based on electrode sensors.

2. APPLICATIONS

Ion-selective electrodes have not yet found extensive use in the analysis of the process materials surveyed in this report. On the other hand, they are being used in closely related situations such as for the analysis and monitoring of industrial wastes. Accordingly, it is reasonable to assume that they could provide advantageous methodology in selected applications. With this in mind, the characteristics of the presently available electrodes are summarized and references are given to applications that are related to, or have some aspects in common with the materials of interest to this report.

A. Cadmium

range: 1M to 10^{-7}M (10 ppb).
pH range of operation: 1 - 14.
interferences: Ag^{+}, Hg^{++}, and Cu^{++} must be absent; Pb^{++} and Fe^{+++} must not exceed Cd^{++} level.

Applications include industrial wastes, plating solutions, non-ferrous alloys, and lubricating oils and greases (3).

B. Calcium

range: 1M to 10^{-5}M (0.4 ppm).
pH range: 5.5 - 11.
interferences (in decreasing order of selectivity): Zn^{++}, Fe^{+++}, Pb^{++}, Cu^{++}, Ni^{++}, Sr^{++}, Mg^{++}, Ba^{++}.

Applications include monitoring of process stream water (hardness), calcium in food processing, and the calcium content of minerals (5, 6).

C. Copper (II)

range: 1M to 10^{-7}M (6 ppb).
pH range: 0 - 14.
interferences: Ag^{+} and Hg^{++} must be absent; Fe^{+++} must be less than 1/10 Cu^{++} level.

Applications include monitoring plating and etching baths for printed circuit manufacture, oil refining processes, industrial and mining waste waters, and determining copper in ores, minerals and alloys (7, 8).

D. Cyanide

range: $10^{-2}M$ to $10^{-6}M$ (0.03 ppm).

pH range: 0 - 14.

interferences: sulfide ion must be absent; iodide should not exceed the cyanide level. To prolong electrode life, an operating range of $\leq 10^{-3}M$ CN^- is recommended.

Applications include monitoring industrial metal extractions and certain petrochemical processes, determination of cyanide in plating baths, rinse tanks, and metal finishing solutions (9).

E. Fluoride

range: 1M to $10^{-6}M$ (0.02 ppm).

pH range: 0 - 9.

interferences: hydroxide ion is the only significant interference: OH^- concentration must not exceed F^- level, i.e., $pOH > pF$.

Applications include monitoring municipal water supplies, electroplating baths, etching and cleaning solutions, pesticides, industrial waste waters, stack gases, and minerals (10-21).

F. Lead

range: 1M to $10^{-7}M$ (0.02 ppm).

pH range: 2 - 14.

interferences: Ag^+, Hg^{++}, and Cu^{++} must be absent from the sample; Cd^{++} and Fe^{+++} must not exceed the Pb^{++} level.

Applications include measurement of lead in electroplating baths, petroleum products, and non-ferrous alloys (22).

G. Silver/sulfide

range: 1M to 10^{-7}M Ag^+ or $S^=$ (0.01 ppm Ag^+; 0.003 ppm $S^=$)

pH range: 0 - 14.

interferences: mercury is the only interference - must be absent from the sample solution.

Applications include measurements of silver or sulfide in industrial process streams and waste waters, e.g., free sulfide detection in the manufacture of paper and pulp (23, 24, 25).

H. Sodium

range: 1M to 10^{-6}M (0.02 ppm)

pH range: 3 - 12.

interferences: the most serious interference is Ag^+ to which the electrode is 10^6 times more sensitive; H^+ is also a serious interference but easily controlled by pH buffering; Li^+, K^+, and NH_4^+ are minor interferences.

Applications include monitoring high-purity boiler water, pulping liquors, and the purification effectiveness of desalination plants (26, 27, 28).

I. Potassium

range: 1M to 10^{-5}M (0.4 ppm).

pH range: 2 - 11.

interferences: major interference from Cs^+ and Rb^+; minor interference from NH_4^+, Na^+, Ag^+, and Li^+.

Applications include monitoring potassium in industrial process streams and in biological fluids (29, 30).

In addition to the above electrodes, several new sensors have recently become available commercially. However, because of the newness of these electrodes, interference data are not yet available. In all cases, one part of an ionic strength stabilizer solution is added to 50 parts of the sample solution. A pH adjustment is then made as required.

Arsenic (V)	range: 1M to 10^{-7}M (8 ppb) pH adjustment: 6-8
Chromium (VI)	range: 1M to 10^{-5}M (0.5 ppm) pH adjustment: none
Mercury (II)	range: 1M to 10^{-7}M (20 ppb) pH adjustment: none
Zinc (II)	range: 1M to 10^{-6}M (0.1 ppm)

3. DISCUSSION

Ion-selective electrodes can be used to determine specific elements precisely and at very low levels if the matrices can be suitably modified or degraded to provide the elements as ions in solution. For most of the matrices under consideration in this survey, such a conversion can be carried out by chemical means, e.g., wet ashing with acids. This chemical pretreatment is time-consuming and often requires considerable skill but in many cases can be automated if large numbers of samples are to be processed.

Once the samples are in the appropriate solution form, the electrode determination is relatively simple and can be performed by a variety of techniques depending on the accuracy and precision desired. Using direct potentiometry or one of the single-increment techniques, imprecisions on one percent to 10 percent can be achieved by most electrodes, if interferences are properly masked, from concentrated solutions to the one ppm level. At the sub-ppm level, precision will degrade due to variable blanks, poor ionic buffering, and slower electrode response. Direct potentiometry or addition methods are rapid, requiring only one to five minutes and are easily portable for field use. For higher precision, 0.1 percent to one percent, titrations or multiple-addition techniques can be used with a concomitant increase in experimental complexity and time required for the analysis (3 to 15 minutes).

A wide range of sample sizes can be analyzed by electrode sensors with the upper limit defined only by homogeneity considerations. With miniaturized electrodes, lower sample volume limits of 1 µl to 10 µl are feasible. For a 10^{-5}M solution, only about one nanogram (10^{-9}g) of sample element is required. The feasibility of such microdeterminations has been reported, e.g., 0.4 ng of fluoride (10 µl) was determined with an accuracy and precision of about one percent using a fluoride electrode (31).

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CHAPTER 10

STANDARD REFERENCE MATERIALS

John K. Taylor

1. INTRODUCTION

Modern instrumental techniques involve measurements in which a known sample is compared with an unknown. This may be a direct comparison or, in the more usual case, an indirect comparison in which the instrument is calibrated with knowns to obtain linear or curvilinear concentration-signal relationships. Such relationships are valid for establishing the composition of unknowns if the calibrants are reliable, and if they simulate the composition of the unknown. In many cases, this simulation must be close to overcome the influence of the matrix on the calibration.

From the foregoing, it is evident that reliable calibrants are a necessity for accurate instrumental analysis. Moreover, matrix-similar reference materials are required to verify the absence of bias in a given analytical situation. Furthermore, it is necessary that such reference materials be of requisite integrity and be available to all to provide a means of intercalibration by all interested parties.

Standard Reference Materials certified by the National Bureau of Standards fulfill all of the above requirements. An SRM is a well characterized material, of proven homogeneity and stability which NBS certifies and distributes for calibration of measurement systems. Approximately 700 substances are presently available for use in a wide variety of analytical situations. Many of these are certified for their trace-element content, and a number of them simulate the process materials of this report.

The analyst involved in trace element analysis of environmentally important materials is well advised to obtain pertinent SRM's which either match or closely simulate his analytical samples. Rather than serving as working standards, these SRM's are best considered as primary standards which can be used to verify the accuracy of a method as it is developed and to a limited extent for quality control purposes. That is, SRM's may be introduced into an analytical sequence, on occasion, to replace or supplement the quality control samples normally used.

SRM's can be invaluable for evaluating analytical procedures during the development process and also in the collaborative testing of proposed procedures, where they can be used as one of the control samples. An analyst who has an occasional need to analyze an unfamilar material will also find an SRM useful to test his competence in a special situation.

The growing interest in trace-element analysis of environmentally important materials has stimulated the development of several SRM's of this nature. The materials available at the time of preparation of this report are reviewed in the following sections of this chapter. These are classified as of direct interest if the matrix closely matches environmentally important substances in the area of this report. There are several SRM's that are of indirect interest because they simulate the analytical problems of the environmental analyst and they have been carefully characterized for their trace element composition. A brief description of all of these SRM's is also included in a following section. Catalogues containing full details and ordering information and cost are available from the Office of Standard Reference Materials, National Bureau of Standards, Washington, D. C. 20234.

2. SRM'S OF DIRECT ENVIRONMENTAL INTEREST

A. Fly Ash

SRM 1633, Trace Elements in Fly Ash, is intended as an analytical standard for the determination of various trace elements in coal fly ash. It consists of a blend of coal fly ash obtained from five electric power plants, selected to cover a broad spectrum of fuel sources from the mining industry. Four of the ashes were collected by electrostatic precipitators and one by a mechanical collector. The material was screened and the portion passing through a 170 mesh sieve was mixed in a double-coned blender.

The certified values given below are based on the analysis of at least a 250 mg sample of the dried material and is the minimum amount that should be used.

Element	Content µg/g
Manganese	493 ± 7
Zinc	210 ± 20
Vanadium	214 ± 8
Lead	70 ± 4
Chromium	131 ± 2
Copper	128 ± 5
Nickel	98 ± 3
Arsenic	61 ± 6
Uranium	11.6 ± 0.2
Selenium	9.4 ± 0.5
Cadmium	1.45 ± 0.06
Mercury	0.14 ± 0.01

The following values are not certified because they are based on a non-reference method, or were not determined by two or more independent methods. They are included for information only.

Element	Content (μg/g)
Potassium	(16800)
Strontium	(1380)
Rubidium	(112)
Cobalt	(38)
Thorium	(24)
Beryllium	(12)
Thallium	(4)

B. Coal

1. Trace Elements in Coal

SRM 1632, Trace Elements in Coal, is intended as an analytical standard for the determination of trace elements in coal. The material is a blend of commercially available coals, obtained from five electric power plants, and selected to cover a broad spectrum of the coal mining industry. The material was reground as needed and screened. The portion passing a 120 mesh sieve but retained on a 325 mesh sieve was taken. The five coals, so processed, were combined and mixed in a double-coned blender.

The certified values given below are based on the analysis of at least a 250 mg sample of the dried material and is the minimum amount that should be used for a determination.

Element	Content μg/g
Iron	8700 ± 300
Manganese	40 ± 3
Zinc	37 ± 4
Vanadium	35 ± 3
Lead	30 ± 9
Chromium	20.2 ± 0.5
Copper	18 ± 2
Nickel	15 ± 1
Arsenic	5.9 ± 0.6
Selenium	2.9 ± 0.3
Uranium	1.4 ± 0.1
Thallium	0.59 ± 0.03
Cadmium	0.19 ± 0.03
Mercury	0.12 ± 0.02

The following values are reported but not certified because they are based on a non-reference method, or were not determined by two or more independent methods (concentrations in $\mu g/g$): Titanium (800); Cobalt (6); Silicon (3.2); Thorium (3.0); Beryllium (1.5).

2. Mercury in Coal

SRM 1630, Trace Mercury in Coal, is available and certified for its content of this environmentally important element. The material is a commercial, low-volatile bituminous coal, ground to a particle size of 210 to 500 micrometers and contains 0.13 parts per million mercury by weight.

The mercury content of the SRM was determined by neutron activation analysis and by flameless atomic absorption spectrometry. In addition, the selenium content was determined and is reported as 2.1 parts per million, but this value is not certified.

3. Sulfur in Coal

SRM 1631 consists of three different low-volatile bituminous coals, ground to pass a 60-mesh sieve, packaged separately. Each coal is certified for its sulfur and ash contents on an as-received basis.

Coal	Sulfur, Percent	Ash, Percent
A	0.546 ± .003	5.00 ± .02
B	2.016 ± .014	14.59 ± .09
C	3.020 ± .008	6.17 ± .02

The methods of analysis used for certifying this material were essentially those identified as ASTM Method D271. Four laboratories, experienced in the analysis of coal, cooperated in the certification of this material and their analytical values were in close agreement with the NBS values which provide the basis of certification.

C. Fuel Oil

1. Trace Elements in Fuel Oil

Work is in progress at NBS on SRM 1634, Trace Elements in Fuel Oil, and it is expected to be released for distribution by June 1975. Certification of the following trace elements is expected: mercury, selenium, zinc, nickel, lead, arsenic, beryllium, manganese, vanadium.

2. Sulfur in Fuel Oil

Three samples of residual fuel oil and a distillate oil are available, certified for their sulfur content. These are representative fuel oils, obtained from a commercial producer. The certified values are as follows:

SRM	Type	Sulfur Content, Weight Percent
SRM 1624	Distillate	0.211 ± .004
SRM 1623	Residual	0.268 ± .004
SRM 1622	Residual	2.14 ± .01
SRM 1621	Residual	1.05 ± .02

The method of analysis used for certification was essentially ASTM Method D-129 in which sulfur is determined gravimetrically as barium sulfate after combustion in an oxygen bomb.

D. Inorganic Materials

A number of SRM's are available in this category. Trace elements are certified in some instances and minor elements in most cases. Those available are listed below.

1. Minerals

Chemical Composition
(Nominal Weight Percent as the Oxide)

SRM	Type	Wt/Unit (grams)	SiO_2	Fe_2O_3	Al_2O_3	TiO_2	MnO	CaO
1b	Limestone, argillaceous	50	4.92	0.75	1.12	0.046	0.20	50.9
88a	Limestone, dolomitic	50	1.20	.28	0.19	.02	.03	30.1
70a	Feldspar, potash	40	67.1	.075	17.9	.01	----	0.11
99a	Feldspar, soda	40	65.2	.065	20.5	.007	----	2.14
97a	Clay, flint	60	43.7	.45	38.8	1.90	----	0.11
98a	Clay, plastic	60	48.9	1.34	33.2	1.61	----	.31

SRM	SrO	MgO	Cr_2O_3	Na_2O	K_2O	Li_2O	ZrO_2	BaO	Rb_2O	P_2O_5	CO_2
1b	0.14	0.36	----	0.04	0.25	-----	-----	-----	----	0.08	40.4
88a	.01	21.3	----	.01	.12	-----	-----	-----	----	.01	46.6
70a	-----	-----	----	2.55	11.8	-----	-----	0.02	0.06	----	----
99a	-----	0.02	----	6.2	5.2	-----	-----	.26	----	.02	----
97a	.18	.15	0.03	0.037	0.50	0.11	0.063	.078	----	.36	----
98a	.039	.42	.03	.082	1.04	.070	.042	.03	----	.11	----

2. Ores

These SRM's are intended for use in checking the accuracy of assay methods. They are certified for their content of elements of economic interest, and occasionally, have additional data given for information only. These SRM's are supplied in the form of fine powders, usually passing a 100-mesh or finer sieve.

SRM	Type	Wt/Unit (Gram)	CaF	Fe	Mn	Li_2O	SiO_2	P_2O_5	P	Available Oxygen
25	Manganese	100	-----	-----	57.85	---	2.36	0.22	-----	16.7
27e	Iron (Sibley)	100	-----	66.58	-----	--	3.65	----	0.042	----
79a	Fluorspar	120	97.39	----	-----	---	----	----	-----	----
113a	Zinc, concentrate	IN PREP								
180	Fluorspar, high-grade	120	98.8	----	-----	---	--	----	-----	----
181	Lithium (Spodumene)	45	-----	-----	-----	6.4	---	----	-----	----
182	Lithium (Petalite)	45	-----	-----	-----	4.3	----	----	-----	----
183	Lithium (Lepidolite)	45	-----	-----	-----	4.1	----	----	-----	----

Chemical Composition
(Nominal Weight Percent as the Oxide)

SRM	Type	Wt/Unit (gram)	Al_2O_3	CaO	P_2O_5	SiO_2	Fe_2O_3	F	CO_2	TiO_2	Na_2O
69a	Bauxite	50	55.0	0.29	0.08	6.01	5.8	----	----	2.78	<0.01
120b	Phosphate Rock (Florida)	90	1.06	49.40	34.57	4.68	1.10	3.84	2.79	0.15	< .35

SRM	MgO	ZrO_2	K_2O	K_2O	Cr_2O_3	SO_3	MnO	V_2O_5	BaO	CdO
69a	0.02	0.18	<0.01	-----	0.05	0.04	0.02	0.03	0.01	-----
120b	.28	----	< .12	0.090	----	----	.28	----	----	0.002

3. Cements

These SRM's are furnished for x-ray spectroscopic analysis and for chemical analysis of cements and related materials. Because these SRM's are hygroscopic, each unit consists of three sealed vials each containing approximately 5 g of material. The supply of the 1011, 1013-1016 Cements will soon be exhausted and replaced with seven new Cements, SRM's 633-639. (Values in parentheses are not certified, but are given for information only.)

Chemical Composition
(Nominal Weight Percent as the Oxide)

SRM	Type	Wt/Unit (grams)	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	P_2O_5
633	Portland B (red)		21.9	3.74	4.2	0.24	0.24
634	Portland C (gold)		20.7	5.2	2.87	.30	.10
635	Portland D (blue)		18.5	6.2	2.65	.32	.17
636	Portland F (yellow)		23.2	3.1	1.62	.17	.09
637	Portland G (pink)		23.1	3.3	1.80	.21	.25
638	Portland I (green)		21.4	4.5	3.58	.25	.06
639	Portland J (clear)		21.6	4.3	2.42	.31	.08
1011	Portland	15	21.03	5.38	2.07	.25	.33
1013	Portland	15	24.17	3.30	3.07	.20	.20
1014	Portland	15	19.49	6.38	2.50	.25	.32
1015	Portland	15	20.65	5.04	3.27	.26	.05
1016	Portland	15	21.05	4.97	3.71	.34	.13

SRM	CaO (+SrO)	SrO	MgO	SO_3	Mn_2O_3	Na_2O	K_2O	Li_2O	Rb_2O	Loss on Ignition
633	64.5	0.31	1.04	2.18	0.04	0.64	0.165			0.75
634	62.6	.12	3.4	2.16	.28	.14	.43			1.61
635	59.8	.22	1.25	7.0	.09	.07	.45			3.25
636	63.5	.04	4.0	2.3	.12	.10	.57			1.16
637	66.0	.10	0.72	2.33	.06	.13	.245			1.68
638	62.1	.07	3.84	2.3	.05	.12	.59			0.95
639	65.8	.15	1.29	2.4	.08	.65	.05			1.0
1011	66.60	.11	1.12	1.75	.03	.08	.26	(0.002)	(0.001)	1.13
1013	64.34	.08	1.39	1.80	.05	.20	.32	(.001)	(.004)	0.99
1014	63.36	.26	2.80	2.70	.07	.24	.99	(.005)	(.007)	.81
1015	61.48	.11	4.25	2.28	.06	.16	.87	(.004)	(.005)	1.70
1016	65.26	.25	0.42	2.27	.04	.55	.04	(.012)	(<.001)	1.20

Chemical Composition
(Nominal Weight Percent as the Oxide)

SRM	Type	Wt/Unit (grams)	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	P_2O_5
633	Portland B (red)		21.9	3.74	4.2	0.24	0.24
634	Portland C (gold)		20.7	5.2	2.87	.30	.10
635	Portland D (blue)		18.5	6.2	2.65	.32	.17
636	Portland F (yellow)		23.2	3.1	1.62	.17	.09
637	Portland G (pink)		23.1	3.3	1.80	.21	.25
638	Portland I (green)		21.4	4.5	3.58	.25	.06
639	Portland J (clear)		21.6	4.3	2.42	.31	.08
1011	Portland	15	21.03	5.38	2.07	.25	.33
1013	Portland	15	24.17	3.30	3.07	.20	.20
1014	Portland	15	19.49	6.38	2.50	.25	.32
1015	Portland	15	20.65	5.04	3.27	.26	.05
1016	Portland	15	21.05	4.97	3.71	.34	.13

SRM	CaO (+SrO)	SrO	MgO	SO_3	Mn_2O_3	Na_2O	K_2O	Li_2O	Rb_2O	Loss on Ignition
633	64.5	0.31	1.04	2.18	0.04	0.64	0.165			0.75
634	62.6	.12	3.4	2.16	.28	.14	.43			1.61
635	59.8	.22	1.25	7.0	.09	.07	.45			3.25
636	63.5	.04	4.0	2.3	.12	.10	.57			1.16
637	66.0	.10	0.72	2.33	.06	.13	.245			1.68
638	62.1	.07	3.84	2.3	.05	.12	.59			0.95
639	65.8	.15	1.29	2.4	.08	.65	.05			1.0
1011	66.60	.11	1.12	1.75	.03	.08	.26	(0.002)	(0.001)	1.13
1013	64.34	.08	1.39	1.80	.05	.20	.32	(.001)	(.004)	0.99
1014	63.36	.26	2.80	2.70	.07	.24	.99	(.005)	(.007)	.81
1015	61.48	.11	4.25	2.28	.06	.16	.87	(.004)	(.005)	1.70
1016	65.26	.25	0.42	2.27	.04	.55	.04	(.012)	(<.001)	1.20

4. Refractories

SRM	Type	Wt/Unit (grams)	Chemical Composition (Nominal Weight Percent as the Oxide) SiO_2	Al_2O_3	Total as Fe_2O_3	FeO	TiO_2
103a	Chrome refractory	60	4.6	29.96	----	12.43	0.22
198	Silica refractory	45	----	0.16	0.66	-----	.02
199	Silica refractory	45	----	.48	.74	-----	.06
104	Burned magnesite	60	2.54	.84	7.07	-----	.03

SRM	ZrO_2	MnO	P_2O_5	Cr_2O_3	CaO	MgO	Li_2O	Na_2O	K_2O
103a	0.01	0.11	0.01	32.06	0.69	18.54	-----	-----	-----
198	<.01	.008	.022	------	2.71	0.07	0.001	0.012	0.017
199	.01	.007	.015	------	2.41	.13	.002	.015	.094
104	----	.43	.057	0.026	3.35	85.67	.001	.015	.015

E. Metals and Alloys

Numerous SRM's are available in this category. They include steels, irons, high-temperature alloys, steelmaking alloys, aluminum-base alloys, cobalt-base alloys, copper-base alloys, lead-base alloys, magnesium-base alloys, selenium-base alloys, tin-base alloys, titanium-base alloys, zinc-base alloys, and zirconium-base alloys.

High purity metals, including gold, platinum, and zinc, available in wire, rod, and massive form, have been certified for their trace-element contents and are recommended especially for the development of new and improved methods and for extension of sensitivity of detection of trace constituents by chemical, optical emission, solid mass spectrometry, and activation analysis. Microprobe standards are also available in the form of iron-chromium-nickel alloys, tungsten-molybdenum alloys, gold-silver alloys, gold-copper alloys, and iron-silicon alloys. These SRM's are certified for their major constituents and are intended to calibrate quantitative electron microprobe analytical techniques.

Because of the large number of SRM's classified under this category, it is not feasible to list their properties here. The catalogue available from the NBS office of Standard Reference Materials should be consulted for details.

F. Metal-Organics

A series of 24 organic materials with high metal content are available as reference materials. These are principally "soaps" of cyclohexanebutyric acid, supplemented by other types of compounds, such as chelates of 1-phenyl-1, 3-butane-dione. These materials are stable, non-volatile, and oil-soluble, so they can be used to prepare solutions in oil. The SRM's presently available are as follows:

SRM	Constituent Certified		Type
	Element	(wt. percent)	
1075a	Al	8.1	Aluminum 2-ethylhexanoate
1051b	Ba	28.7	Barium cyclohexanebutyrate
1063a	B	2.4	Menthyl borate
1053a	Cd	24.8	Cadmium cyclohexanebutyrate
1074a	Ca	12.5	Calcium 2-ethylhexanoate
1078b	Cr	9.6	Tris(1-phenyl-1,3-butanediono)chromium(III)
1055b	Co	14.8	Cobalt cyclohexanebutyrate
1080	Cu	16.5	Bis(1-phenyl-1,3-butanediono)copper(II)
1079b	Fe	10.3	Tris(1-phenyl-1,3-butanediono)iron(III)
1059b	Pb	36.7	Lead cyclohexanebutyrate
1060a	Li	4.1	Lithium cyclohexanebutyrate
1061c	Mg	6.5	Magnesium cyclohexanebutyrate
1062a	Mn	13.8	Manganous cyclohexanebutyrate
1064	Hg	36.2	Mercuric cyclohexanebutyrate
1065b	Ni	13.9	Nickel cyclohexanebutyrate
1071a	P	9.5	Triphenyl phosphate
1066a	Si	14.1	Octaphenylcyclotetrasiloxane
1076	K	10.1	Potassium erucate
1077a	Ag	42.6	Silver 2-ethylhexanoate
1069b	Na	12.0	Sodium cyclohexanebutyrate
1070a	Sr	20.7	Strontium cyclohexanebutyrate
1057b	Sn	23.0	Dibutyltin bis(2-ethylhexanoate)
1052b	V	13.0	Bis(1-phenyl-1,3-butanediono)oxovanadium(IV)
1073b	Zn	16.7	Zinc cyclohexanebutyrate

3. SRM'S OF INDIRECT ENVIRONMENTAL INTEREST

The SRM's classified under this heading are of interest in that their analysis simulates many of the problems encountered in environmental samples. All of them have been widely used by trace analysts so that their reliability is well established. The use of such SRM's in the course of an analytical program thus provides a means to correlate analytical measurements with those obtained in other fields, hence they serve as valuable reference materials where direct interest materials are not available, and are supplemental materials in other cases.

A. Trace Elements in Glass

A series of four glasses containing a variety of trace elements in the 0.02 to 500 ppm range have been prepared and provide excellent reference material for determination of trace-elements in refractory inorganic matrices. The matrix is a soda-lime glass with the following nominal composition: 72 percent SiO_2; 12 percent CaO; 14 percent Na_2O; 2 percent Al_2O_3.

The material was prepared by addition of the trace elements to the melt which was mixed, then extruded in the form of a rod. The reference materials consist of wafers sliced from the rod and can be obtained in two thicknesses - 1 mm, and 3 mm. Some 35 elements are certified or reported in these glasses while 26 other elements are known to be present.

The glasses are homogeneous in composition, from wafer-to-wafer, but there is some radial segregation. The certificate describes the limitations on their use.

SRM Trace Elements in Glass

SRM	Type — Matrix	Size	Unit of Issue
608	Trace Elements in Glass, Set	**Wafers** 3 mm Diameter	Set: 2 each 614 and 616
609	Trace Elements in Glass, Set	**Wafers** 1 mm Diameter	Set: 2 each 615 and 617
610	Trace Elements in Glass, 500 ppm . . .	**Wafers** 3 mm Diameter	6 Wafers
611	Trace Elements in Glass, 500 ppm . . .	**Wafers** 1 mm Diameter	6 Wafers
612	Trace Elements in Glass, 50 ppm	**Wafers** 3 mm Diameter	6 Wafers
613	Trace Elements in Glass, 50 ppm	**Wafers** 1 mm Diameter	6 Wafers
614	Trace Elements in Glass, 1 ppm	**Wafers** 3 mm Diameter	6 Wafers
615	Trace Elements in Glass, 1 ppm	**Wafers** 1 mm Diameter	6 Wafers
616	Trace Elements in Glass, 0.02 ppm . . .	**Wafers** 3 mm Diameter	6 Wafers
617	Trace Elements in Glass, 0.02 ppm . . .	**Wafers** 1 mm Diameter	6 Wafers
618	Trace Elements in Glass, Set	**Wafers** 3 mm Diameter	Set: 1 each 610, 612, 614 and 616
619	Trace Elements in Glass, Set	**Wafers** 1 mm Diameter	Set: 1 each 611, 613, 615 and 617

Element	606	607	610–611 500 ppm	612–613 50 ppm	614–615 1 ppm	616–617 0.02 ppm
Antimony.	-----	-----	-----	-----	(1.06)	(0.078)
Barium	-----	-----	-----	(41)	-----	-----
Boron.	-----	-----	(351)	(32)	(1.30)	(0.20)
Cadmium	-----	-----	-----	-----	(0.55)	-----
Cerium	-----	-----	-----	(39)	-----	-----
Chromium	-----	-----	-----	-----	(0.99)	-----
Cobalt	-----	-----	(390)	(35.5)	0.71	-----
Copper	-----	-----	(444)	(37.7)	1.34	(0.65)
Dysprosium . . .	-----	-----	-----	(35)	-----	-----
Erbium	-----	-----	-----	(39)	-----	-----

SRM Trace Elements in Glass (contd)

Element	606	607	610–611 500 ppm	612–613 50 ppm	614–615 1 ppm	616–617 0.02 ppm
Eurpoium	-----	-----	-----	(35)	(0.99)	-----
Gadolinium	-----	-----	-----	(39)	-----	-----
Gallium	-----	-----	-----	-----	(1.3)	(0.23)
Gold	-----	-----	(25)	(5)	(0.5)	(0.18)
Indium	-----	-----	-----	-----	(0.75)	(0.26)
Iron	-----	-----	458	51	13.5	(11)
Lanthanum	-----	-----	-----	(36)	(0.83)	(0.034)
Lead	(0.374)	-----	426	38.57	2.32	1.85
Manganese	-----	-----	485	(39.6)	(1.41)	(0.65)
Molybdenum	-----	-----	(111)	-----	-----	-----
Neodymium	-----	-----	-----	(36)	-----	-----
Nickel	-----	-----	458.7	38.8	(0.95)	-----
Potassium	-----	-----	(461)	(64)	30	29
Rhenium	-----	-----	(49.1)	-----	-----	-----
Rubidium	-----	523.90	425.7	31.4	0.855	(0.0998)
Samarium	-----	-----	-----	(39)	-----	-----
Scandium	-----	-----	-----	-----	(0.59)	(0.026)
Silver	-----	-----	(254)	22.0	0.42	-----
Strontium	-----	65.485	515.5	78.4	45.8	41.72
Thallium	-----	-----	(61.8)	(15.7)	(0.269)	(0.0082)
Thorium	-----	-----	457.2	37.79	0.748	0.0252
Titanium	-----	-----	(437)	(50.1)	(3.1)	(2.5)
Uranium	-----	-----	461.5	37.38	0.823	0.0721
Ytterbium	-----	-----	-----	(42)	-----	-----
Zinc	-----	-----	(433)	-----	(2.43)	-----

In addition to the 35 elements listed above, the Glass SRM's contain the following 26 elements: As, Be, Bi, Ca, Cl, F, Ge, Hf, Hg, Li, Lu, Mg, Nb, P, Pr, Se, S, Ta, Te, Tb, Tm, Sn, W, V, Y, and Zr.

B. Orchard Leaves

SRM 1571 Orchard Leaves was intended for use in the calibration of apparatus and methods used in the analysis of agricultural and other botanical materials for major, minor, and trace elements. However, because of the variety of elements certified, and the fact that it closely simulates the kind of sample often obtained in environmental measurements, such as those collected for particulate analysis, it has been widely used for analytical methodology investigations.

The elements listed below have been determined by at least two analytical techniques and the uncertainties represent those due to analytical measurement and homogeneity of a 250 mg sample.

	Element	Content		
A.	Major Constituents	Wt. Percent		
	Nitrogen	2.76	±	0.05
	Calcium	2.07	±	0.03
	Potassium	1.47	±	0.03
B.	Minor Constituents	Wt. Percent		
	Magnesium	0.62	±	0.02
	Phosphorous	0.21	±	0.01
C.	Trace Constituents	μg/g		
	Iron	300	±	20
	Manganese	91	±	4
	Sodium	82	±	6
	Lead	45	±	3
	Boron	33	±	3
	Zinc	25	±	3
	Arsenic	14	±	2
	Copper	12	±	1
	Rubidium	12	±	1
	Nickel	1.3	±	0.2
	Mercury	0.155	±	0.015
	Cadmium	0.11	±	0.02
	Selenium	0.08	±	0.01
	Uranium	0.029	±	0.005

In addition to the above elements, the following elements have been determined but their content is not certified because of minor analytical problems or because they have been measured by only one technique: bismuth, bromine, chlorine, chromium, cobalt, fluorine, lithium, strontium, sulfur.

The analytical techniques used in the certification of this material included: atomic absorption spectroscopy; flame emission spectroscopy; isotope dilution mass-spectrometry; neutron activation analysis; polarography; optical emission spectroscopy; photon activation analysis; nuclear track technique.

C. Bovine Liver

SRM 1577 Bovine Liver is the first animal tissue material certified by NBS for its trace element content. It is useful not only to those concerned with the effects of trace elements from environmental pollution, but as a general trace element standard where a predominantly organic matrix is present.

The material is certified for the following elements:

Element	Content
	(Wt. Percent)
Nitrogen	10.6 ± 0.6
Potassium	0.97 ± 0.06
Sodium	0.243 ± 0.013
	(µg/g)
Iron	270 ± 20
Copper	193 ± 10
Zinc	130 ± 10
Rubidium	18.3 ± 1.0
Manganese	10.3 ± 1.0
Selenium	1.1 ± 0.1
Lead	0.34 ± 0.08
Cadmium	0.27 ± 0.04
Mercury	0.016 ± 0.002

In addition to the above elements, the contents of the following are reported but not certified because only one technique was used in their determination: arsenic; calcium; chlorine, cobalt; magnesium; molybdenum; silver; strontium; thallium; uranium.

SUPPLEMENTAL REFERENCES

Because of space limitations, the chapter references have been limited to those directly concerned with the subject matter of this document. However, many additional references were collected and reviewed and the decision for rejection was often difficult. Accordingly, some of those of considerable peripheral interest are given below to provide supplemental information of a general or specific nature. The titles of the papers are descriptive of their contents.

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